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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

The Band Spectrum of Mercury. ERNST LIESE (*Zeitsch. wiss.
Photochem.*, 1912, 11, 349—375).—The banded spectrum of mercury
s readily obtained when the uncondensed discharge from an induction
oil is passed through a discharge tube in which mercury is distilled
from one end to the other. In addition to the bands described by
Eder and Valenta, which are situated at the more refrangible end of
the spectrum, the author has observed other bands stretching from
the green to the red end. These bands appear to be of an inter-
mittent character, and although visual observations indicate that
their structure is similar to that of the bands at the violet end of the
spectrum, it has not been possible to obtain satisfactory photographs
of them.

Wave-length measurements have been made in the case of four of
the more refrangible bands, and the band structure thus indicated is
discussed in reference to the formulæ of Deslandres and Ritz. In
neither case do the calculated frequencies agree satisfactorily with
those corresponding with the series of lines actually observed in the
banded spectrum. H. M. D.

**Magnetic Resolution of the Spectra of Nickel, Cobalt,
and Iron.** (Mlle.) I. M. GRAFTDYE (*Arch. Néerland*, 1912, [iiiA], 2,
192—220).—The resolution of the lines which occurs when a

magnetic field is applied has been investigated in a quantitative manner. For iron, the spectral region examined extends from $\lambda = 4500$ to $\lambda = 6500$, for nickel from $\lambda = 2300$ to $\lambda = 6300$, and for cohalt from $\lambda = 3300$ to $\lambda = 4200$. If H denotes the strength of the applied field, then $d\lambda/\lambda^2 H$ affords a measure of the magnetic resolution, and if this is plotted against the number of the resolved lines, a curve is obtained which represents the frequency with which a given effect is produced. The great majority of the lines give rise to triplets, hut the quantitative data afford no evidence of the existence of definite series of lines. In regard to the above-mentioned frequency curves, which are very irregular in character, there appear to be maxima for values of $d\lambda/\lambda^2 H$ equal to $10\cdot75$ and $14\cdot25 \times 10^{-13}$ in the case of iron, and when this quantity is equal to $10\cdot50$, $11\cdot00$, and $13\cdot25 \times 10^{-13}$ in the case of nickel. Between these values and the normal resolution of $9\cdot4 \times 10^{-13}$ there appears to he no simple connexion. The frequency curve for cohalt shows no very pronounced maxima.   H. M. D.

Normal and Anomalous Zeeman Effects. FRIEDRICH PASCHEN and E. BACK (*Ann. Physik*, 1912, [iv], **39**, 897—932).—The resolution hrought about hy a magnetic field has been examined in the case of certain oxygen, helium, hydrogen, lithium, sodium, and potassium lines. The observations are discussed with reference to the general relationships which have heen found in connexion with the magnetic resolution of series lines.   H. M. D.

A New Proof of the Existence of Molecules. V. NILS PIHLBLAD (*Zeitsch. physikal. Chem.*, 1912, **81**, 417—430. Compare A., 1909, ii, 277, 561, 723; 1910, ii, 946).—A continuation of the work of Svedberg and Pihlblad. Colloidal solutions, suspensions, and molecular solutions of coloured dyes were made containing particles of varying sizes, and the light absorption investigated. The suhstances used were anilino blue-2B, indophenol-P, azobenzene, Bordeaux-R, and fast-red-A. Tho methods adopted for varying the size of the particles were: (1) addition of alkali, (2) addition of a protecting colloid (for example, rubber), (3) progressive mechanical suh-division, and (4) ageing the solutions. It is shown that here as in the former work (*loc. cit.*) that the light ahsorption curves of the disperse systems approach those for molecular solutions as the size of the particles is decreased. With increasing size of the particles the ahsorption curves show a flattening.   J. F. S.

Relationship between Fluorescence and Chemical Constitution. JOHANNES STARK (*Zeitsch. Elektrochem.*, 1912, **18**, 1011—1014).—Polemical, and contains a survey of the publications of H. Kauffmann made at the "Deut. Bunsen-Ges. Vers." held at Karlsruhe (*ibid.*, 481). The author opposes the view that fluorescence is a property depending in any way on molecular constitution, and cites evidence to show that it is rather an atomic property. The interpretation of the luminous effects obtained, by Kauffmann, in gases hy the use of Tesla oscillations is adversely criticised.
                                                        J. F. S.

A New Method for Examining Optically Active Compounds: Anomalous Dispersion. Leo A. Tschugaev (*J. pr. Chem.*, 1912, [ii], 86, 545—550).—A criticism of Deussen's work (A., 1912, ii, 510, 1020) on this subject.

The author refers to his own investigations, and points out that he has previously proposed that the rotatory dispersion of optically active compounds may be utilised for their analysis. 　　　F. B.

The [Chemical] Efficiency of Light Energy. Fritz Weigert (*Zeitsch. wiss. Photochem.*, 1912, 11, 381—394).—The author has collected and examined the available experimental observations relating to the chemical efficiency of the light which is absorbed in photo-chemical reactions. The values of the photochemical yield for the various reactions are summarised in the following table :

| | Percentage yield estimated. | |
Photochemical reaction.	Thermo-chemically.	Thermo-dynamically.
Carbon dioxide assimilation	98 and 14—20	—
Anthracene $\longrightarrow$ dianthracene	—	4·5
$S_\lambda \longrightarrow S_\mu$	0·24	—
Decomposition of ammonia	2·0	0—2
Formation of ozone	46·0	27·7

　　　　　　　　　　　　　　H. M. D.

Photo-electric Action of the Extreme Ultra-violet on Water, Aqueous Solutions, and Ice. W. Obolensky (*Ann. Physik*, 1912, [iv], 39, 961—975).—Experiments are described which show that water is photo-electrically sensitive to ultra-violet rays of very short wave-length. The ultra-violet light was obtained from the spark discharge between aluminium electrodes, and by the interposition of screens of fluorspar, quartz, air, calcspar, glass, and gypsum, it was possible to eliminate portions of the ultra-violet spectrum in a series of stages. In this way it has been found that the most active rays are those of the extreme ultra-violet region in the neighbourhood of $\lambda = 130\,\mu\mu$. For this group of rays, the photo-electric activity of water is about 1/400th of that of cupric oxide. As the wave-length increases, the exciting power of the rays falls off very quickly, and vanishes completely when λ exceeds 202·5 $\mu\mu$.

The addition of small quantities of acids, bases, and salts has no appreciable influence on the photo-electric activity of water. In larger quantities, chlorides diminish the effect, whilst sulphates, carbonates, and nitrates increase it. The presence of the dissolved salts also causes a displacement of the spectral position of the rays which exert the maximum effect.

Ice is much more photo-electrically sensitive than water. For the unfiltered rays from the aluminium spark discharge, its activity is about 0·7 of that of cupric oxide, and for the group of rays in the neighbourhood of $\lambda = 180\,\mu\mu$, it surpasses cupric oxide in its sensitiveness. Experiments with hoar-frost show that this behaves very similarly to ice.

The meterological significance of the observations is referred to.
H. M. D.

Photo-electric Effect of Some Compounds. R. S. WILLOWS (*Phil. Mag.*, 1912, [vi], **24**, 891—892).—According to Hughes (A., 1912, ii, 880), dry zinc chloride shows no photo-electric activity, although photo-electric currents of considerable intensity are obtained with the moist substance. This observation is probably connected with the fact that the moist halogen salts of zinc emit large quantities of positive and negative ions when heated to 300°, whereas the dried salts are inactive (compare Garrett, A., 1907, ii, 524). The halogen salts are evidently unstable, and ultra-violet radiation in presence of moisture represents one of several agents, the action of which suffices to bring about decomposition. H. M. D.

· **Inversion of Sucrose by Ultra-violet Rays.** HENRI BIERRY, VICTOR HENRI, and ALBERT RANC (*Compt. rend.*, 1912, 155, 1151—1153. Compare A., 1911, i, 524).—A claim for priority over Berthelot and Gaudechon (compare A., 1910, ii, 813 ; 1912, ii, 1120) for the discovery of the inverting action of ultra-violet rays on sucrose, the inversion being a direct result of the action of these rays. W. G.

Photolysis of Different Classes of Sugars by Ultra-violet Light. DANIEL BERTHELOT and HENRI GAUDECHON (*Compt. rend.*, 1912, 155, 1153—1156. Compare A., 1912, i, 750 ; ii, 715, 1120).—The simple sugars can be divided into four classes according to their resistance to light ; the ketoses are attacked by ultra-violet rays ($\lambda > 0.30\mu$), the aldoses by the rays ($\lambda = 0.30$ to 0.25μ), the straight-chain polyhydric alcohols by rays ($\lambda = 0.25$ to 0.20μ), and the ring polyhydric alcohols only by the extreme ultra-violet rays ($\lambda > 0.20\mu$). With light of slow vibrations, producing the first stage in the action, the liquid remains neutral, and does not reduce Fehling's solution in the cold. Then, with more rapid vibrations, decomposition increases, the liquid becomes acid, and carbon dioxide can be detected in the gaseous products ; the amount of hydrogen evolved increases, the solution begins to reduce Fehling's solution in the cold, and finally methane is liberated. The volumes of carbon monoxide and hydrogen evolved in the first stage always bear a simple ratio to one another. The results of a series of comparative experiments are given, and it is found that, in the case of the ketoses, the solid sugars as well as their aqueous solutions undergo decomposition. W. G.

Secondary γ-Rays Excited by the β-Rays of Radium. FREDERICK SODDY (*Phil. Mag.*, 1912, [vi], **24**, 892).—Remarks on Chadwick's paper (A., 1912, ii, 1025) calling attention to a prior publication (A., 1910, ii, 474). F. S.

The Energy of the Groups of β-Rays from Radium. ERNEST RUTHERFORD (*Phil. Mag.*, 1912, [vi], **24**, 893—894).—In the paper by the author (A., 1912, ii, 1024) the energy of the β-particle was calculated from the formula $E = \frac{1}{2}m_0 C^2 (\beta^2 / \sqrt{1 - \beta^2})$, where m_0 is the " slow-

speed mass," C the velocity of light, and β the ratio of the velocity of the β-particle to that of light. The correct formula should have been $E = m_0 C^2(1/\sqrt{1-\beta^2}) - 1$, which nearly agrees with the former for small values of β, but departs widely as β approaches unity. The $pE_1 + qE_2$ relation of the former paper holds with the new formula; only E_1 and E_2 have new values, namely, $E_1 = 1\cdot12 \times 10^{13}e$, and $E_2 = 0\cdot356 \times 10^{13}e$; p has values between 0 and 9, and q between 0 and 2. The twelve lines between Nos. 21 and 9 fit in, with the exception of No. 11. For lines Nos. 1 to 8, there is an approximately constant energy difference, $E_3 = 0\cdot173 \times 10^{13}e$, which is nearly $\frac{1}{2}E_2$. These lines are due probably to radium-B, whilst line No. 9 may be due to either -B or -C. The calculated energy required to excite characteristic X-radiation in an atom of atomic weight 214 is for the "K" type $1\cdot27 \times 10^{13}e$, and for the "L" type $0\cdot19 \times 10^{13}e$ ergs, numbers which do not greatly differ from the values of E_1 and E_3.　　　　　　　　　　　　　　　F. S.

The Ratio of the Intensities of the Hydrogen Canal Ray Lines. FRITZ LUNKENHEIMER (*Ann. Physik*, 1912, [iv], 39, 1071).— In reference to Stark's criticism of the results obtained by the author (A., 1911, ii, 950), it is pointed out that these have been confirmed by Vegard (*Ann. Physik*, 1912, [iv], 39, 111).　　　　　　　H. M. D.

Luminosity of Gases under the Influence of Cathode Rays. II. ERNST GEHRCKE and R. SEELIGER (*Ber. Deut. physikal. Ges.*, 1912, 14, 1023—1031. Compare A., 1912, ii, 517).—An improved form of apparatus is described for the study of the luminosity of gases subjected to the action of cathode rays of gradually diminishing velocity. The effect of the alterations which have been made is to increase the length of the path over which the cathode particles give rise to characteristic luminosity from a fraction of a millimetre to several millimetres. The colour effects obtained with nitrogen, hydrogen, helium, argon, mercury, carbon monoxide, and coal gas are described. In general, three differently coloured regions of luminosity are discernible, the best results being obtained in the case of hydrogen, whilst the regions are least sharply differentiated in helium. The spectra of the different regions have been examined for hydrogen, nitrogen, helium, and mercury, and these observations indicate that the colour changes brought about by the action of the retarded cathode rays are dependent on the specific characters of the luminous particles.

By comparison of the above luminous effects with those found in the positive column of the glow discharge, it is found that the sequence of colours is not always the same, although in many cases the individual colours are identical.　　　　　　　　　　　　　　H. M. D.

Spectra of Low Potential Discharges in Air and Hydrogen. GORDON S. FULCHER (*Physikal. Zeitsch.*, 1912, 13, 1137—1142).—An examination has been made of the spectrum of the light emitted by the action of slowly moving cathode rays on the molecules of nitrogen, hydrogen, and oxygen. With a sufficiently hot Webnelt cathode, with the electrodes about 5 cm. apart and a gas pressure of about 0·1 mm. of mercury, it has been found that discharge may be effected when the

potential difference amounts to 20 volts in the case of hydrogen, 27 volts in air, and 45 volts in oxygen. The spectra of the low potential discharge are compared with those obtained in the case of high speed cathode rays. The observations with air indicate that the small speed cathode rays give rise only to the emission of the positive nitrogen bands. Between 30 and 50 volts the relative intensity of the negative bands increases, however, very rapidly with the energy of the exciting rays, and at higher potentials the intensity becomes much greater than that of the positive bands. The difference in the behaviour of the two kinds of rays may be due to the more complete penetration of the molecules by the high speed rays. As an alternative explanation it is suggested that the positive bands are emitted by molecular aggregates which are dissociated by the high speed, but not by the low speed rays.

Similar differences are found when the low and high potential discharge spectra are compared, and the intensities of different lines in the two spectra are shown in a comparative table.   H. M. D.

The Emission of Negative Corpuscles by Certain Salts which have Previously been Subjected to [Cathode] Rays. M. VOLMER (*Zeitsch. Elektrochem.*, 1912, 18, 1086—1090).—The author has repeated the experiments of Henriot (*Ann. Chim. Phys.*, 1912, [viii], 26, 134) and finds that he is unable to confirm them, whilst at the same time the work of McLennan is confirmed (A., 1902, ii, 297). The power of emitting negative corpuscles, after treatment with cathode rays, is restricted to comparatively few salts, including K_2SO_4, Na_2SO_4, Li_2SO_4, $CaSO_4$, $BaSO_4$, and $SrSO_4$, whilst amongst those examined which did not possess this property are KCl, KBr, KI, $BaCl_2$, $KHSO_4$, Na_2SeO_4, $(NH_4)_2SO_4$, $MgSO_4$, $K_2Cr_2O_7$, KCN, CaO, and CaS. The author directs attention to the fact that, whereas McLennan (*loc. cit.*) got an effect with the alkaline earth sulphides amounting to one-fifth that obtained with K_2SO_4, he was unable to obtain any effect whatever, and he suggests that the sulphides used by McLennan contained sulphate. The rate at which the emission of corpuscles falls off does not follow the simple exponential law, but it is found to agree very well with an empirical law of Becquerel (*La lumière*, p. 295) for the decrease of phosphorescence. $J^n(c+t)=c$, in which n has value lying between $\frac{1}{2}$ and 1. An hypothesis is propounded to explain the action; it assumes that a decomposition of the salts is brought about by the cathode rays. Two cases are differentiated: (1) in which the components are driven apart and remain as isolated entities in the mass of the substance; (2) in which the components remain within the spheres of influence of one another. In the latter case the components combine instantaneously as soon as the rays are stopped and emit at the same time a negative corpuscle, whereas in the former case the components can only recombine as diffusion brings them within the spheres of influence of one another, and this would naturally occur more quickly, and consequently a more rapid emission of corpuscles would occur, at higher temperatures. The hypothesis certainly fits the experimental facts.
                                                                    J. F. S.

Effect Produced by a Magnetic Field on Ionisation Currents. WILLIAM DUANE (*Le Radium*, 1912, 9, 342—347).— Experiments on the effect of magnetic fields on the movements of ions have been carried out with a view to deciding whether positive electrons exist in ionised gases. A narrow pencil of α-rays from a thin-walled tube of radium emanation passed between the plates of an ionisation chamber, placed between the poles of a magnet, such that the lines of force were normal to the path of the rays and to the electric force between the plates. The whole apparatus was capable of being exhausted very perfectly, so as to increase the free paths of the ions. There is always an enormous difference in the effect of the magnet on the positive and negative currents. For the currents carried by the negative ions the field diminishes the current even at pressures of several cm. of mercury, whilst at 0·06 mm., both in hydrogen and air, a field of a few hundred gausses reduces the current to a small fraction of 1%. For the positive current in air no effect is detectable at pressures above 0·03 mm. At pressures of a few thousandths of a mm. and an electric field not above 10 volts, a magnetic field of 1000 gausses diminished the current perceptibly in air, but, with an electric field of 25 volts, even a magnetic field of 2600 gausses produced no effect.

In hydrogen the effect of the magnetic field is more marked. From Sir J. J. Thomson's theory an estimate of the mass of the ions is formed from the experiments, although a precise measurement of e/m is not possible. All the negative ions are corpuscular, and none of them can be formed by the separation of a molecule into oppositely charged parts of molecular order of magnitude. In air the value of e/m for the positive ion is less than 740 and 500 in two experiments, which is in agreement with the view that the ions are atoms and molecules of oxygen and nitrogen, for which the values of e/m would be 612, 700, 306, and 350, assuming unit charge. For hydrogen the numbers are much greater than for air, and a large proportion have values for e/m greater than 700.   F. S.

The Chemical Action of Penetrating Radium Rays. III. The Influence of the Penetrating Rays on Some Inorganic Compounds. ANTON KAILAN (*Monatsh.*, 1912, 33, 1329—1359. Compare A., 1912, ii, 522).—Under the influence of the penetrating radium rays the following reactions have been observed. Ferric sulphate is reduced, the reduction being considerably increased in the presence of sucrose (compare Ross, A., 1906, ii, 512). The formation of hydrogen peroxide from water takes place both in acid, neutral and alkaline solutions, the amount formed being greatest with acidified and least with alkaline water. No difference is observed whether the vessel containing the water be coated with paraffin or not.

In sulphuric acid solution, potassium bromide is decomposed with the liberation of bromine. The velocity of decomposition does not increase in direct proportion to the increase in concentration of the bromide or acid, since when the concentration of either the salt or the acid is increased ten-fold, the velocity of decomposition is only increased by about one-half. Under similar conditions, the rate of

liberation of bromine from solutions of potassium bromide is only about one-twentieth to one-hundredth of that of the liberation of iodine from solutions of potassium iodide (compare A., 1912, ii, 522), when the action of any hydrogen peroxide which may be formed is neglected. Any formation of hydrogen peroxide would lead to too great a difference in the observed rates of decomposition of solutions of potassium iodide and bromide.　　　　　　　　T. S. P.

The Chemical Action of Penetrating Radium Rays. IV. The Influence of the Penetrating Rays on Some Organic Compounds and Reactions. ANTON KAILAN (*Monatsh.*, 1912, 33, 1361—1377).—The influence of the penetrating radium rays has been studied in the following cases : the catalytic action of hydrochloric acid on the velocity of esterification of benzoic acid, either in absolute or aqueous alcoholic solution, is not affected, from which the conclusion may be drawn that there is also no effect on the dissociation of alcoholic hydrochloric acid.

The formation of acid from *o*-nitrobenzaldehyde is accelerated, both in alcoholic and benzene solution ; the increase in the rate of reaction with increasing concentration of the aldehyde is hardly appreciable.

Neither in ethereal nor in alcoholic solution have 100 mg. of radium chloride any action on *p*-benzoquinone, nor is the light reaction accelerated.

Solutions of oxalic acid are not affected at 25°, but the rate of inversion of unsterilised solutions of sucrose is accelerated, the acceleration increasing with increasing length of time of the experiment. Acid is formed by the action of the rays, and the extent of the inversion corresponds approximately with the amount of acid formed. The growth of mould in unsterilised sucrose solutions seems to be favoured by the action of the rays.　　　　　　　　T. S. P.

Evidence that Sodium belongs to a Radioactive Series of Elements. F. C. BROWN (*Le Radium*, 1912, 9, 352—355).—The term "radioactive element" is employed to include, not only elements undergoing atomic disintegration, but also the products of such disintegration, such as helium, and the attempt is made to show from geological evidence that sodium is a member of a radioactive series. The data derived from the quantities of lead and of helium in radioactive minerals give estimates of the age of these minerals greatly in excess of the estimate, between 6·5 and 10×10^7 years, derived from the quantity of sodium in the ocean. Accepting the higher estimate from radioactive data, the small quantity of sodium can be explained by supposing either that a parent of sodium exists in the earth, but not in the ocean, or that the sodium in the ocean, in absence of its parent, is in process of diminution by disintegration. The hypothesis explains the fact that there is a great relative excess of chlorine over sodium in the ocean, whereas in the rivers the opposite is the case. The parent of sodium is to be sought among those elements more abundant in the earth than in ocean deposits.　　　　　　　　F. S.

Radioactivity of the Springs at Vichy and Other Places.
A. LABORDE and ADOLPHE LEPAPE (*Compt. rend.*, 1912, 155, 1202—1204. Compare Curie and Laborde, A., 1904, ii, 461; 1906, ii, 515).—The authors have measured the radioactivity of the waters and gases from eight springs at Vichy, and springs at several other sources, and have also determined the quantity of radium in the deposits and residues from evaporation of these waters, the results being tabulated. The deposits from a number of the springs were further examined for thorium, it being absent in four cases and in two cases present to the extent of 0·11 to 0·50%, or about one hundred times more that in the common rocks. W. G.

The Action of the Silent Electric Discharge on a Mixture of Hydrogen and Titanium Tetrachloride. I. F. BÖCK and LUDWIG MOSER (*Monatsh.*, 1912, 33, 1407—1429).—Pure dry hydrogen is passed through titanium tetrachloride, and the gas, charged with the vapours, is submitted to the action of a silent electric discharge in a specially designed apparatus. At the ordinary temperature the walls of the apparatus became coated with a dark brown deposit, the reactions of which showed it to contain titanium trichloride, although it was not the pure substance, containing also some tetrachloride. In different experiments the composition of the deposit varied considerably, but on heating in a vacuum at 100° the tetrachloride could be distilled off, leaving the trichloride as a brown substance, in which the tetrachloride had been probably occluded. This brown substance is probably a labile, allotropic form of the ordinary violet titanium trichloride, since it changes into the latter when heated at 150—200° in a vacuum.

For experiments at temperatures above 200°, neither glass nor porcelain apparatus could be used, since the electric discharge penetrated them. An apparatus was, however, designed in which the solid dielectric consisted of mica, which was wrapped in thin sheets round a glass tube. This could be used for temperatures between 200° and 400°, but not higher; at these temperatures the pure anhydrous violet trichloride was obtained, the stable modification apparently having no tendency to occlude the tetrachloride. T. S. P.

The Glow Discharge in Very Pure Gases. GEORG GEHLHOFF (*Ber. Deut. physikal. Ges.*, 1912, 14, 960—969).—Experiments are described which show that the stratification of the positive glow which occurs in the passage of the discharge through nitrogen and the inert gases is dependent on the presence of traces of impurities. When these are removed, the positive glow is continuous. In the case of hydrogen, the formation of strata cannot, however, be eliminated by purification of the gas, and the phenomena would therefore appear to depend in the case of the pure gases on the electrical character of the gas molecules.

The changes which occur in the discharge potential and in the cathode potential when a discharge is passed through a tube containing potassium vapour have been found to be due to the purification of the residual gas by the alkali metal and to the covering of the cathode with a layer of metallic potassium. H. M. D.

An Attempt to Determine the Dielectric Cohesion of a Rare Gas, with Small Quantities of Material. EDMOND BOUTY (*Compt. rend.*, 1912, 155, 1207—1208. Compare A., 1911, ii, 458).— By slightly altering his apparatus, the author has been able to make measurements on 5—6 c.c. of gas instead of the 200 c.c. ordinarily required. The relation of the apparent value, B, so obtained to the true value, b, for the dielectric cohesion is given by $B = 1\cdot165b + 6$, which calibration with helium, neon, and air shows to be applicable from $b = 7$ to $b = 419$. Provided that the volume of the gas is not too small and that the pressure is sufficiently great, the value, γ, of the field capable of producing visible illumination in the gas is a linear function of the pressure. The apparatus can be used in following the stages of purification of a rare gas. W. G.

Electrical Resistance Measurements of Mixtures of Copper and Mercury. A. P. SCHLEICHER (*Zeitsch. Elektrochem.*, 1912, 18, 998—1000).—The alloys examined were made in the first series of experiments by threading a number of amalgamated copper wires through a long glass tube, the spaces between the wires being filled with mercury. In this way an alloy, in which the two components could be regarded as arranged like separate wires in close contact, was imitated. The results show that for alloys in which the components are longitudinally arranged, the resistance is a linear function of the volume composition. In the second series the alloys were imitated by placing a number of short pieces (1 cm.) of amalgamated wire into the tube and filling the interstices with mercury. This arrangement represents a more or less fine-grained crystalline alloy. The results show that the relation between the volume composition and the conductivity in a linear one, but it is regarded as unlikely that such a relationship will hold for the resistance. J. F. S.

Electrical Conductivity of Copper–Tin Alloye (a Correction). R. LEDOUX (*Compt. rend.*, 1912, 155, 1249).—A correction of two temperature-coefficients for Cu–Sn alloys, the values of which, as given in a previous paper (compare A., 1912, ii, 727), were incorrect. W. G.

Variation of the Conductivity of Aluminium Anode Films with Temperature. G. E. BAIRSTO (*Trans. Faraday Soc.*, 1912, 8, 232—252. Compare A., 1912, ii, 123).—Further experiments with aluminium anode films confirm the exponential law of variation of conductivity with temperature, $i = A\epsilon^{a\vartheta}$, the value of a being independent of the time of formation, the concentration of the electrolyte, and the nature of the cation, whilst A depends on these factors. The value of a varies with the anion, and serves as a measure of the equivalent of the anion. The conductivity of a film is about constant for voltages up to about one-half of the voltage of formation, and rapidly increases at higher voltages. At temperatures above 60°, the current-voltage curves have a maximum at a voltage below that of

formation. When log i is plotted against θ, the cooling curve lies above the heating curve, but becomes parallel with it.   C. H. D.

Relative Electrical Conductivity and Ionisation of Aqueous Solutions of Hydrogen Chloride between 18° and 81°. Joseph A. Muller (*Bull. Soc. chim.*, 1912, [iv], 11, 1001—1006. Compare A., 1911, ii, 266).—The conductivity of aqueous solutions of hydrogen chloride has been determined at 18°, 51°, and 81°, the concentrations at the first temperature being accurately determined and those at the higher temperatures deduced from the coefficients of expansion of the solutions employed. In each case, a solution of maximum conductivity was observed, the molecular concentrations of which expressed with respect to the concentration of acid at 18° were respectively, $C_{18} = 5.77$ at 18°, $C_{18} = 5.88$ at 51°, and $C_{18} = 5.98$ at 81°, corresponding approximately with 19.6 grams of hydrogen chloride in 100 grams of solution. The ionisation of aqueous solutions of hydrogen chloride was found to diminish rapidly with increasing concentration of acid, but, for a definite concentration, to vary but little with the temperature.

                                                H. W.

Conductivity, Temperature-coefficients of Conductivity, and Dissociation of Certain Electrolytes in Aqueous Solution at 35°, 50°, and 65°. S. F. Howard and Harry C. Jones (*Amer. Chem. J.*, 1912, 45, 500—536).—In continuation of earlier work (Hosford and Jones, A., 1911, ii, 960; Winston and Jones, A., 1911, ii, 961), conductivity measurements have been made at 35°, 50°, and 65° of aqueous solutions of sodium ferrocyanide, potassium carbonate, potassium permanganate, dipotassium hydrogen phosphate, potassium sodium sulphate, potassium chromium sulphate (violet and green), potassium nickel sulphate, ammonium chromium sulphate (violet and green), calcium bromide, calcium chromate, zinc nitrate, zinc acetate, lead chloride, lead acetate, nickel acetate, uranyl chloride, uranyl nitrate, uranyl sulphate, uranyl acetate, hydrochloric acid, nitric acid, and sulphuric acid. The molecular conductivities, temperature-coefficients, and percentage dissociation are tabulated.

Jones and MacKay (A., 1897, ii, 396) found that the conductivities for certain of the alums were not constant, but changed with time. This explains certain discrepancies between some of the results of the present investigation and those obtained in the earlier work. It has been found that the time factor for hydrolysis is greater for concentrated than for dilute solutions, and that the temperature has but little effect on it. The observation that salts containing large amounts of water of crystallisation have large temperature-coefficients is confirmed. In the case of salts which do not undergo hydrolysis, the temperature-coefficients increase with dilution. The violet forms of ammonium and potassium chrome alum have smaller conductivities than the green forms, but the difference becomes less at higher temperatures. In several instances, hydrolysis was observed; dipotassium hydrogen phosphate had a time factor which extended over several days. With the exception of uranyl acetate and dipotassium

hydrogen phosphate, the percentage dissociation decreased with rise of temperature; the phosphate acted normally after being left for four weeks.   E. G.

The Electrical Conductivity of Solutions in Methylamine and Ethylamine; The Fluidity of Ammonia, Methylamine and Sulphur Dioxide, and the Fluidity of Certain Solutions in these Solvents. FRED F. FITZGERALD (*J. Physical Chem.*, 1912, 16, 621—661. Compare Franklin, A., 1911, ii, 1052).—The abnormal conductivity-dilution curves given by solutions in methyl.amine, ammonia, and liquid sulphur dioxide have been further investigated in conjunction with the viscosities and densities of the solvents and a number of their solutions.

Solutions of silver nitrate and potassium iodide in methylamine at $-33.5°$, $-15°$, $0°$, and $+15°$ have a maximum of molecular conductivity at about normal concentration, followed by a minimum at $N/40$, and then a progressive rise on further dilution. There is no evidence that the molecular conductivity tends to approach a maximum value at high dilutions as in the case of aqueous solutions of these substances. Some hitherto unpublished conductivity measurements by D. H. Hoagland on solutions of potassium iodide, lithium nitrate, lithium chloride, sodium nitrate, mercuric iodide, and m-dinitrobenzene in methylamine are given. With the exception of the values given by m-dinitrobenzene his results are of the same general character.

Solutions of silver nitrate, ethylammonium chloride, and lithium chloride in ethylamine have a maximum of molecular conductivity at about normal strength, followed by an asymptotic diminution on dilution, but although the dilution was carried to $N/100$ in the case of silver nitrate the molecular conductivity showed no tendency to increase again.

The temperature-coefficient of conductivity of solutions in methyl.amine and ethylamine changes sign on passing from concentrated to dilute solutions, as has already been observed with certain solutes in sulphur dioxide and ammonia. The solvent and ionising properties of the amines are related to those of ammonia as the properties of the alcohols to those of water. On ascending the homologous series of solvents the ionising power and the solvent action on metallic salts decreases, but the solvent action on carbon compounds increases.

The densities and fluidities at $0°$ of solutions in methylamine and ammonia of potassium iodide, lithium chloride, sodium nitrate, silver nitrate, silver iodide, carbamide, sucrose, m-methoxybenzenesulphonamide, 2 : 4-dinitroaniline, ammonium bromide, and copper nitrate were measured in a special form of Ostwald viscometer. The viscosities of these solutions decrease progressively on dilution, and the author does not attempt to trace any connexion between his conductivity and viscosity measurements.

The viscosities, η, of the pure solvents methylamine, ammonia, and sulphur dioxide were also measured. The values of the product $\eta\Lambda_\infty$, where Λ_∞ is the molecular conductivity of potassium iodide at infinite dilution, fall between 0·9 and 1·1 with ammonia and sulphur dioxide, whereas with normal solvents Walden obtained the value 0·65.

Ammonia and sulphur dioxide must therefore be regarded as abnormal in the same sense as water is abnormal. R. J. C.

Electro-capillary Pulsation of a Mercury Meniscus. ALEXANDER P. ROSHDESTWENSKY and WILLIAM C. McC. LEWIS (*Trans. Faraday Soc.*, 1912, 8, 220—231).—The most sensitive solution for use in a capillary electrometer is the ordinary sulphuric acid solution, but in the course of experiments with various electrolytes it has been found that when mercuric cyanide is used regular pulsations of the mercury surface are observed within certain ranges of potential difference (above one volt, the mercury in the capillary being the cathode) and with concentrations of $N/10$ and upwards. The period is of the order of thirty seconds, suggesting that adsorption layers are built up and destroyed. C. H. D.

The Peltier Effect and the Iron–Mercury Thermo-electric Couple. E. OOSTERHUIS (*Arch. Néerland*, 1912, [IIIA], 2, 7—38).— The magnitude of the Peltier effect at the surface of contact between iron and mercury has been measured by a calorimetric method at a series of temperatures extending from that of the room to 182°. Corresponding determinations were also made of the thermo-electric potential difference, E, the influence of temperature on which may be expressed by the equation : $E.10^7 = 169.53t - 0.06336t^2 - 0.00008918t^3$. The Peltier effect, π, representing the heat change due to the passage of one ampere for one second through the contact surface, increases from 116.44×10^{-5} cal. at 18.5° to 151.1×10^{-5} cal. at 182.3°. From the two series of data it is found that the relationship $\pi = T.dE/dT$ is satisfied within the limits of experimental error. On the other hand, the equation $\sigma_1 - \sigma_2 = -T.d^2E/dT^2$, in which σ_1 and σ_2 represent the Thomson effects for the mercury and iron respectively, is quite inconsistent with the experimental data. From this it follows that the energy of the thermo-electric current cannot be accounted for on the basis of the energy changes corresponding with the Thomson and Peltier effects. H. M. D.

Electro-chemical Behaviour of Tantalum. GEORG VON HEVESY and ROLAND E. SLADE (*Zeitsch. Elektrochem.*, 1912, 18, 1001—1002).— The potential differences between tantalum and a solution of tantalum pentafluoride (0·006 mol.) were measured both with passive tantalum and active tantalum. The values Ta (passive) | TaF_5 | $= +1.537$ volt and Ta (active) | TaF_5 | $= +0.165$ volt, were obtained ($H = 0$).

The authors arrive at the conclusions, that in its most passive condition tantalum has a nobler potential than silver of about 1 volt, whilst active tantalum has a potential close to that of copper.

J. F. S.

New Fuel Batteries. EMIL BAUR and H. EHRENBERG (*Zeitsch. Elektrochem.*, 1912, 18, 1002—1011. Compare A., 1910, ii, 573, 574). —Several new fuel batteries have been investigated with respect to their *E.M.F.*, current output, internal resistance, and polarisation. The batteries are constructed in porcelain ∪-tubes embedded in

magnesia and heated by an alternating current. The cells all consist of an oxygen electrode, maintained by leading oxygen or air continuously into molten silver. The fuel electrodes consist of carbon rods, or metal tubes (iron, nickel, platinum, or copper), into which hydrogen or carbon monoxide is continuously led. The electrodes dip into molten electrolytes, which in the various cases are: potassium carbonate, sodium carbonate, and mixtures of the two, also potassium metasilicate, cryolite and alumina, and borax.

The cell $C \mid NaKSiO_3 + KF \mid O_2, Ag$ has an $E.M.F.$ of 1·11 volt, which is raised to 1·24 volt by leading hydrogen into the carbon compartment of the cell; the internal resistance is approximately one ohm, and the cell is polarised to the extent of about 20% when furnishing a current of 500 amperes per sq. metre of carbon surface. The hydrogen cells $H_2 \mid Na_2B_4O_7 \mid O_2, Ag$ gave at 1000° different values for the $E.M.F.$, depending on the nature of the tube through which the gas diffused; a copper tube gave 0·84 volt; an iron tube, 1·007 volt; nickel tube, 0·93 volt. Incidentally it is shown that 30 litres of hydrogen diffuse through 1 sq. metre of iron in one hour at 1000°, and 69 litres through nickel under the same conditions. The carbon monoxide cells $CO \mid Na_2B_4O_7 \mid O_2, Ag$ at 1000° gave with a platinum tube for the intake of the gas an $E.M.F.$ of 0·61 volt, with a copper tube, 0·65 volt, and a nickel tube, 0·80 volt.

The carbon cells were investigated on the large scale, since it was decided that the polarisation was due to the relatively small quantity of silver and, consequently, lack of oxygen for the process. The following results are given: Cell $C \mid Na_2B_4O_7 \mid O_2, Ag$ at 1000° had an internal resistance of 0·5 ohm, of which 0·28 ohm is due to the carbon rod and the nickel wire connected to the silver. The $E.M.F.$ on open circuit is 1·002 volt. A series of $E.M.F.$ values for different outputs of current is given. The cell

$$C \mid 14\%Al_2O_3 + 86\%Na_3AlF_6 \mid O_2, Ag$$
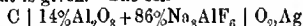
at 1000° has an internal resistance of 0·29 ohm, of which 0·2 ohm is due to the electrolyte; the $E.M.F.$ on open circuit is 0·73 volt. The cell $C \mid Na_2CO_3 \mid O_2, Ag$ at 1000° has internal resistance, 0·165 ohm; $E.M.F.$ on open circuit, 0·92 volt. The cell

$$C \mid 90\%K_2SiO_3 + 10\%KF \mid O_2, Ag$$
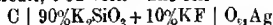
has internal resistance 0·46 ohm; $E.M.F.$ 1·0 volt on open circuit. The whole of the large cells were free from polarisation after several hours' working at a comparatively large current output. Calculations are given to show that the observed $E.M.F.$ values approach very nearly to those theoretically possible.   J. F. S.

Self-induction in Concentration Cells. CHARLES M. VAN DEVENTER (*Chem. Weekblad*, 1912, **9**, 973. Compare A., 1911, ii, 693).—A further contribution to the author's theory of the "leaking insulator," in which he deals with a private communication from J. J. van Laar.   A. J. W.

The Elimination of Potential due to Liquid Contact. II. A Simple Equation for the Calculation of the Diffusion Potential. ALEXANDER C. CUMMING (*Trans. Faraday Soc.*, 1912, **8**, 86—93. Compare A., 1908, ii, 253).—A modification of Henderson's

equation for the diffusion potential (A., 1907, ii, 426 ; 1908, ii, 665) is proposed, applicable in special cases, but it is not possible to simplify the equation in the same way when the anion and the cation of any salt in the system have different valencies. The mobilities of the ions are taken at the experimental concentrations instead of, as in the original equation, at infinite dilution. The only data required are the conductivities and the migration ratios. The equation is tested by comparison with experimental results.　　C. H. D.

New Experiments on the Super-tension of Hydrogen. ALFRED THIEL and E. BREUNING (*Chem. Zentr.*, 1912, ii, 1894 ; from *Festschr. med. naturwiss. Ges.*, 1912, 148—159).—By an elaboration of Caspari's method for the estimation of super-tension (A., 1900, ii, 7), the following values for hydrogen have been obtained. On blank platinum, $0.06—0.08$; on platinised platinum, 0.0000 ± 0.0001 ; on gold, 0.0165 ± 0.0005 ; silver, 0.097 ± 0.002 ; nickel, 0.1375 ± 0.0005 ; copper, 0.1365 ± 0.0005 ; palladium, 0.0000 ± 0.0001.　　J. C. W.

The Polyiodides. II. Periodic Phenomena in the Electrolysis of Solutions of the Alkali Iodides. ROBERT KREMANN and R. SCHOULZ (*Monatsh.*, 1912, 33, 1291—1304).—Küster (A., 1905, ii, 698) has observed periodic phenomena during the electrolysis of solutions of sodium sulphide, and explained them by the formation of insulating deposits of sulphur on the anode, which are dissolved off again when the current strength is low, with the formation of polysulphides ; the current strength again rises, depositing sulphur, and so on. If such an explanation is correct, similar phenomena should be observed during the electrolysis of solutions of the alkali iodides, iodine being temporarily deposited on the anode and then dissolved with the formation of polyiodides.

Using a registering apparatus similar to that employed by Küster, it was found that solutions of cæsium and rubidium iodides gave sometimes regular and sometimes irregular periods of the current intensity ; with potassium iodide very small periods were observed, whilst sodium and lithium iodides gave no periods. With solutions of ammonium iodide, it is doubtful whether periodicity occurs.

The tendency of the alkali iodides to form polyiodides decreases in the order : cæsium, rubidium, ammonium, potassium, and lithium or sodium (Abegg and Hamburger, A., 1906, ii, 747), which is in accordance with the above observations.　　T. S. P.

Electrolysis in Liquefied Sulphur Dioxide. LANCELOT S. BAGSTER and BERTRAM D. STEELE (*Trans. Faraday Soc.*, 1912, 8, 51—67).—The sulphur dioxide is dried by distillation through a long column of phosphoric oxide. When potassium or sodium iodide is electrolysed in this solvent, sulphur is always deposited on the cathode, and potassium or sodium sulphite is also formed in its neighbourhood, corresponding with the formation of a hydroxide at the cathode in aqueous solutions. Gas is not evolved in the absence of moisture.

When a solution of tetramethylammonium iodide in sulphur dioxide is electrolysed at $-35°$ in a vacuum, a dark red solution is formed at

the cathode. A special form of apparatus is used for the purpose of examining the cathode and anode solutions separately. The dark liquid contains tetramethylammonium sulphite, together with an unstable reducing substance, the nature of which is unknown. When a zinc anode is used, mixing the cathode and anode solutions gives a yellow precipitate of *zinc tetramethylammonium sulphite*,

$$Zn_3(NMe_4)_2(SO_3)_4.$$
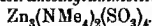
Solutions of hydrogen bromide in sulphur dioxide do not conduct, but conductivity is produced by the addition of water, only a little of which dissolves, the remainder falling to the bottom as a hydrate of hydrogen bromide. The conductivity is attributed to the formation of an oxonium compound. Hydrogen sulphide does not form a corresponding conducting solution. Experiments have been made in which substances capable of forming oxonium compounds with hydrogen bromide, such as ether and dimethylpyrone, are added to the solution, the results indicating that the compound is in most cases slowly formed. The electrode potentials of several metals when immersed in saturated solutions of their salts in sulphur dioxide have also been measured, lead, zinc, and cadmium salts being sufficiently soluble for the purpose.   C. H. D.

The Thermo-electric Properties of the System Iron–Nickel–Carbon. Eugène L. Dupuy and A. Portevin (*Compt. rend.*, 1912, 155, 1082—1085. Compare Steinmann, A., 1900, ii, 523, 524).—The thermo-electric power of a number of nickel steels, annealed or tempered, has been measured between −78·5° and 0°, and between 0° and 100°, by Broniewski's method (compare A., 1912, ii, 258). Curves are given showing the variation of the *E.M.F.* with the percentage of nickel in the steel, and they exhibit a marked minimum corresponding to the change martensite −→ austenite. This variation in thermo-electric power with nickel content could serve as a control for the chemical analysis.   W. G.

Electric Furnace for Experiments in a Vacuum at Temperatures up to 1500°. Roland E. Slade (*Proc. Roy. Soc.*, 1912, *A*, 87, 519—524).—The furnace consists essentially of a platinum tube, 2 cm. diameter, 17·5 cm. long, and with walls 1 mm. thick, each end of the tube being mounted in a water-cooled brass terminal. The tube is heated by the current from an accumulator battery of twelve cells arranged in six parallel sets of two, the furnace requiring about 350 amperes at 3 volts to raise the temperature to about 1400°. It is found that the temperature can easily be kept constant within 1° for several hours at any desired temperature up to 1500°.

In order to permit of the exhaustion of the strongly heated platinum tube, the furnace and its fittings are placed in an enclosure, the pressure in which can be adjusted so as to be nearly the same as that inside the furnace tube.   H. M. D.

The Hall Effect in Metals at Low Temperatures and the Theory of Magnetism from the Point of View of the Theory of Quanta. Hans Alterthum (*Ann. Physik*, 1912, [iv], 39, 933—960).—The influence of temperature on the Hall effect has

been investigated for a number nf metals at temperatures varying from the ordinary temperature to that of liquid hydrogen. The effect of temperature varies according to the nature of the metal, maxima being exhibited hy the curves representing the behaviour of copper, cadmium, antimony, and gold, minima by the curves for aluminium and platinum, whilst in the case nf iron and nickel the Hall effect diminishes with fall of temperature tn 83° ahs., and then remains constant down to 20° ahs.

These differences indicate that the Hall effect is very complex in character, and that it cannot be explained solely on the basis nf the action of the magnetic field on the motion of the free electrons. The assumption that the Hall effect is dependent nn the diamagnetic character of the metal is found to he at variance with some of the ohservations recorded. In the case of the ferromagnetic metals there also appears to he no essential connexion hetween the Hall effect and the internal magnetic fields.

It is further shown that the occurrence of the Hall effect in liquid metals is very improbahle. H. M. D.

Magnetisation of Water and Oxygen. PIERRE WEISS and AUGUSTE PICCARD (Compt. rend., 1912, 155, 1234—1237).—The coefficient of magnetisation of water has been obtained by measuring the attraction or repulsion produced by a specially constructed electromagnet on a quartz tube, suspended from a delicate balance and filled in turn with hydrogen, water, and a solution of manganese chloride. The value obtained for the coefficient of magnetisation for unit mass of water was $\chi = -0{\cdot}7209 \times 10^{-6}$ at 20° with a temperature-coefficient $+0{\cdot}00013$ in the neighbourhood of 20°. The value for oxygen was obtained by measuring the alteration in level of water successively under hydrogen and oxygen, and found to be $\chi = +1{\cdot}0568 \times 10^{-4}$ at 20° for unit mass. W. G.

The Magnetic Properties of Alloys. SIR ROBERT HADFIELD, EDWARD COLVER-GLAUERT, SIEGFRIED HILPERT, PIERRE WEISS, H. KAMERLINGH ONNES, EDGAR WEDEKIND, FRIEDRICH HEUSLER, E. TAKE, ALEXANDER D. ROSS, and THEODOR DIECKMANN (Trans. Faraday Soc., 1912, 8, 94—210).—A series of papers on the general question of magnetic alloys, mainly summarising work previously published (comparo following abstracts). C. H. D.

Magnetic Properties of Iron-Carbon and Iron–Silicon Alloys. ERNST GUMLICH and PAUL GOERENS (Trans. Faraday Soc., 1912, 8, 98—114).—The same percentage nf carbnn in the form of free cementite diminishee the electrical conductivity of iron less than when present as pearlite, and aleo prnduces much less .magnetic hardening. In hardened steele, the saturation value diminishes regularly with increasing carhon. In the higher carhon allnys, therefore, the coercive force increases with increasing quenching temperature.

The improvement of the magnetic qualitiee nf iron by small quantities of silicon is unexplained. With 3 or 4% of silicon, pearlite is decomposed intn ferrite and temper-carbnn, and, even with rapid

cooliug, the formation of the solid solution of carhon in iron is prevented.   C. H. D.

The Magnetic Properties of Special Steels at Low Temperatures. JAMES G. GRAY and ALEXANDER D. ROSS (*Trans. Faraday Soc.*, 1912, **8**, 115—133).—Specimens of steels containing chromium, silicon, phosphorus, or tungsten in addition to carbon have been examined magnetically at the ordinary temperature and at -190°, after annealing and also after quenching from 450° and 900°. Cooling to -190° usually lowers the permeability for low values of the magnetising force and raises it for high values, so that the magoetisation curves at 15° and -190° cross. The crossing point moves to higher values of the field strength with increasing carhon, or with the increase of any other added element. This holds good for quenched as well as for annealed specimens.   C. H. D.

The Heusler Alloys. A. A. KNOWLTON and O. C. CLIFFORD (*Trans. Faraday Soc.*, 1912, **8**, 195—206).—A description of the magnetic properties of nine different ternary alloys of copper, manganese, and aluminium under different conditions of thermal treatmeot. It is not yet known under what condition the alloy of maximum magnetisaticn may be obtained. The hypothesis preferred is that which regards the magnet units in Heusler alloys as complex molecular groups containing at least two different kinds of crystal molecules.   C. H. D.

Magnetic Susceptibility of Ferric Salts. RUDOLF H. WEBER (*Chem. Zentr.*, 1912, ii, 695—696; from *Sitzber. naturf. Ges. Rostock*, 1912, [ii], 4. Compare A., 1906, ii, 331).—For comparison a solution of manganese sulphate (0·10273 gram, per c.c., D^{20} 1·0944) was used. The ferrio sulphate used had the formula $Fe_2(SO_4)_3$; its solutions containing a few drops of sulphuric acid gave lower figures for atomic magnetic susceptibility than those previously recorded (Liebknecht and Wills, A., 1900, ii, 187). Addition of sulphuric acid raised the magnetic susceptibility, as did also gradual dilution. The lowest and highest values found for χ were 0·7521 and 1·008. The addition of $1—2\%$ by volume of sulphuric acid raised the value in one case from 0·8673 to 0·9415, and further addition of hydrogen peroxide produced no effect. A solution having the mimimal value 0·7521 gave 0·9353 on addition of $1—2\%$ sulphuric acid with hydrogen peroxide. The addition of this small amount of sulphuric acid changed the colour from brown to yellow.   T. A. H.

Specific Heat of Substances at Low Temperatures. JACQUES DUCLAUX (*Compt. rend.*, 1912, **155**, 1015—1016).—A theoretical paper in which the author discusses the hypothesis that the diminution of specific heat of the elements at low temperatures, which is very rapid at -200°, is due to the fact that the elements undergo polymerisation at these temperatures.   W. G.

The Dissociation Pressure and Melting Points of the System Copper-Cuprous Oxide. ROLAND E. SLADE and F. D. FARROW (*Proc. Roy. Soc.*, 1912, *A*, **87**, 524—534).—The investigatiou of the

melting-point diagram for mixtures of copper and cuprous oxide has shown that two liquid layers are formed at temperatures above 1195°. At this temperature, the co-existing liquids contain respectively 20·2% and 94·54% of cuprous oxide. From analyses of the two layers obtained by quenching mixtures heated to higher temperatures, it appears that the composition changes only to a small extent with rise of temperature. The actual change observed is in the direction of an increase in the mutual miscibility of the two layers.

With the aid of the tube furnace described previously (this vol., ii, 16), the authors have measured the equilibrium pressures determining the co-existence of the three phases—liquid 1, liquid 2, and gas. The values recorded are 4 mm. at 1205°, 10 mm. at 1240°, 12 mm. at 1260°, and 25 mm. at 1324°. From the data at 1205° and 1260°, the heat of dissociation is calculated to he −90060 cal., and from the data at 1260° and 1324°, −55890 cal. From these numbers it is obvious that the heat of dissociation varies with the temperature, a result which is to be expected in view of the change in composition of the two liquid phases.   H. M. D.

Cryoscopic Determinations in Iodine. ERNEST BECKMANN (*Zeitsch. anorg. Chem.*, 1912, **77**, 200—208).—The material to be added is compressed to form tablets, either alone or with iodine. The constant found is 210, the value 253·5 (Timmermans, A., 1906, ii, 429) being too high. The theoretical value is found to be 201·4. The following molecular formulæ are found : SnI_4, SbI_5, AsI_5, HgI_2, Al_2I_6. Potassium iodide has a normal molecular weight in dilute solution, but polymerises at higher concentrations. Cæsium, sodium, and lithium iodides are polymerised at all concentrations.

C. H. D.

Polymorphism. EFISIO MAMELI and ANNA MANNESSIER (*Gazzetta* 1912, **42**, ii, 566—582. Compare Mameli, A., 1910, ii, 182).—The authors have determined the cryoscopic constants of the α- and β- modifications of chloroacetic acid, using naphthalene, *cyclo*hexanone, o-nitrobenzoic acid, butyric acid, propionic acid, *p*-xylene, *m*-cresol, safrole and acetic acid, and find them to be identical within the limits of experimental error (the means being $K_α$ 52·41, $K_β$ 51·67). Hence both have the value which, according to van't Hoff's formula, should belong to the α-form only.

The molecular weights of water, phosphoryl chloride, aniline, pyridine, and quinoline dissolved in the β-form have also been determined, the results being similar to those obtained with the α-form (*loc. cit.*).   R. V. S.

Cryoscopic Researches. ÉMILE BAUD (*Bull. Soc. chim.*, 1912, [iv], 11, 945—950).—The formula given by Luginin and Dupont (A., 1912, ii, 1040) implies that in paracetaldehyde the lowering of freezing point due to the solution of a second substance is proportional to the molecular concentration. This is only true for certain solvents within certain limits of concentration, and a study of mixtures of (*a*) toluene and ethylene dihromide and (*b*) toluene and hromoform shows

that the formula given by Baud and Gay (A., 1910, ii, 689) agrees better with the experimental results and is more generally applicable. Where heat changes occur on admixture, the heat of dilution must be taken into account, and for such cases an equation has been given already (A., 1912, ii, 233). Such cases are illustrated in this paper by curves for mixtures of acetic acid with (a) benzene and (b) ethylene dibromide.   T. A. H.

Thermal Constants of Camphor. JOUNIAUX (*Bull. Soc. chim.*, 1912, [iv], **11**, 993—1001).—The author finds that the value, 500, previously adopted for the cryoscopic constant of camphor is slightly too high, and prefers the figure 495.   From this, he deduces the value 8·24 cal. for the latent heat of fusion of camphor, whilst from considerations of the vapour tension of camphor at various temperatures, the number 8·23 cal. is obtained.   Further, by the application of Trouton's formula, the latent heat of vaporisation is calculated to be 93·47 cal.   This value is confirmed by two series of calculations, the one based on the vapour tension of liquid camphor, the other on the density of camphor vapour (compare Vanstone, T., 1910, 97, 4).   From the number so obtained, the ebullioscopic constant is calculated to be 49·7 by use of van't Hoff's formula, and confirmation of this value is deduced from Vanstone's experiments (*loc. cit.*) on the vapour tension of camphor and borneol and of the solid solution of these two substances.   H. W.

Ebullioscopy of Iodine. ERNST BECKMANN (*Zeitsch. anorg. Chem.*, 1912, **77**, 275—281).—Ebullioscopic determinations may be made with liquid iodine by using a jacket of boiling aniline.   Mixed platinum and silver beads are used in the inner vessel, silver beads alone becoming cemented by a layer of silver iodide.   The mean ebullioscopic constant of iodine (b. p. 184°) is 105.   Tin, antimony, and bismuth dissolve in the monatomic form, whilst aluminium and iron dissolve as Al_2I_6 and Fe_2I_6, whereas all other solutions indicate a molecule FeI_3.   Alkali iodides give values which are more nearly normal than in the cryoscopic tests (this vol., ii, 19), but a tendency to give high values is still observed, especially in sodium and lithium iodides.   C. H. D.

Vapour-Pressure of Concentrated Aqueous Solutions. EDGAR P. PERMAN and TUDOR W. PRICE (*Trans. Faraday Soc.*, 1912, **8**, 68—85).—The vapour pressure of concentrated aqueous solutions of carbamide, glycerol, eucrose, raffinose, potassium chloride, and calcium chloride has been determined over a range of concentration at temperatures of 70° and 90°.   The air-current method (*Proc. Roy. Soc., A*, 72) is employed.   The lowering of the vapour pressure is proportional to the concentration, except at very high concentrations.   Babo's law holds good in many cases.   Hydration is found to be a function of the concentration.   C. H. D.

Triple Point of Methane. C. A. CROMMELIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 666).—The temperature and pressure at which solid, liquid, and gaseous methane co-exist have been found to

be −183·15° and 7·0 cm. of mercury.   A previous determination by
Olszewski gave −185·8° and 8·0 cm.   H. M. D.

The Critical Coefficient and the Molecular Weight of
Substances at the Critical Point.   A. BOUTARIC (*Compt. rend.*,
1912, **155**, 1080—1082).—A mathematical paper in which the author
discusses the relationship between the critical coefficient and the
molecular weight of a substance.   Taking the value $b/v = 1·20$ as a
mean of thirty determinations, where b is the constant in van der
Waals' equation and v the molecular volume at the boiling point, he
shows that if the value rises above 1·2, the substance must be con-
sidered as polymerised at its critical point.   This is the case for water,
alcohol, and thiophen.   W. G.

The Limit of Formation of Endothermic Compounds at
Very High Temperatures.   EMIL BRINER (*Compt. rend.*, 1912, **155**,
1149—1151).—A theoretical paper in which the author, taking the
values for the heat of formation of molecules from atoms as found for
various elements by different observers, shows that compounds said to
be endothermic will become exothermic at temperatures sufficiently
elevated, and their concentration will reach a maximum and then
diminish with further rise in temperature.   Taking the case of nitric
oxide and applying van't Hoff's equation : $(dlnK_1)/(dT) = -Q_1/(RT^2)$,
he shows that, when the temperature is sufficiently high for the
molecules of nitrogen and oxygen to be completely dissociated, then
the concentration of the nitric oxide will diminish with rise in
temperature.   W. G.

The Behaviour of Iodine and Sulphur at Extremely High
Temperatures, from Explosion Experiments.   NIELS BJERRUM
(*Zeitsch. physikal. Chem.*, 1912, **81**, 281—297).—The vapours of iodine
and sulphur were investigated at temperatures between 3404° and
2299°.   The experiments were conducted by mixing hydrogen iodide
and hydrogen sulphide respectively with known amounts of electro-
lytic gas and exploding the mixture in a steel bomb of about 10 litres
capacity.   The maximum pressure generated by the explosion was
determined by the displacement of a steel membrane, which was
photographically recorded.   Very full working details of the
apparatus are given in the paper, and from the experiment with
hydrogen iodide it is shown that the heat of formation of the
molecule I_2 from its atoms is 35700 calories at temperatures in the
region of 3000°, as compared with 34340 calories obtained by
Bodenstein and Starck at 1000° (A., 1911, ii, 20).   The atomic heat
of iodine vapour is found to be slightly less than 3 at 3000°, the
mean value obtained from many experiments and corrections, intro-
duced for reasons given, is $3·1 \pm 0·3$ between 0° and 3000°.   This value,
being so near to the theoretical figure for monatomic gases, is held
to show that, even at such high temperatures, the gaseous molecules
have only translational energy, and no rotational energy as might
have been expected for such a heavy atom as iodine.   A series of
results for sulphur is recorded, but it was found impossible to deduce

any trustworthy figures from them, since it is shown that at high temperatures a reaction occurs between sulphur vapour and water with the formation of sulphur dioxide.   J. F. S.

Heat of Formation of Some Organic Fluorine Compounds. IV. FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1912, 481—523).—A study of the heat of combustion of various fluorinated phenols, anilines, and aromatic nitro-compounds with a view to determining the influence of these groups on the variation of the internal energy of a compound produced by the replacement of hydrogen by fluorine. Owing to the difficulty of preparing *o*-fluoro-derivatives in any quantity, a complete study of the effect of position isomerism was not possible. The increase in heat of formation caused by the replacement by fluorine of one atom of hydrogen in benzene is 14 calories (compare A., 1907, ii, 9 ; 1908, ii, 354). The presence of a nitro-group has a depressing effect reducing this value to 8 to 9 calories. The introduction of a second nitro-group meta to the first still further reduces the figure to 7·2 calories, whereas *m*-dinitrobenzene shows an increase of 0·8 calorie over nitrobenzene, the fluorine being absent. The presence of an hydroxyl group causes an increase in this figure, the heat of formation of *m*-fluorophenol exceeding that of phenol by 23 calories, this being the value previously obtained with aliphatic hydrocarbons (*loc. cit.*). In the case of the phenols it was possible to study the effect of the position of the —OH group relative to the fluorine atom. The meta-derivative shows the highest increase, the para- being second, whilst in the ortho-position the —OH group has no effect whatever on the increase in the heat of formation. The replacement of the hydroxyl hydrogen by ethyl diminishes by 3 calories the increment value due to the —OH group in the meta- and para-isomerides.

In the case of the substituted anilines, the amino-group causes a rise in the increased value of the heat of formation, the meta-isomeride again giving a higher value than the para. This difference, however, practically disappears in the case of the acetanilides.

A few tri-substituted benzene derivatives have also been examined, but no very definite conclusions could be drawn from the results, except that the nitro-group, in the ortho-position to the fluorine, still exerts a strong depressing effect on the heat of formation. Two aliphatic nitro-compounds were also examined, and a similar lowering in the heat of formation due to the nitro-group was proved in both cases.

Full numerical data are tabulated. A description of the preparation and proporties of a number of new fluoro-compounds, used for this work but not as yet described, will shortly be published in a separate communication.   W. G.

Thermochemical Researches on Solution. NICOLAS KOLOSOVSKI (*Bull. Acad. roy. Belg.*, 1912, 591—609 *).—The author gives a brief résumé of the various theories of solution, and then proceeds to a thermochemical examination of the problem by determining the heat of solution of sodium chloride in aqueous solutions of

* and *J. Russ. Phys. Chem. Soc.*, 1912, 44, 1659—1674.

alcohol, this solvent being his example of a binary mixture. The measurements were made in a Berthelot calorimeter, the alcohol used being purified by treatment with calcium oxide and potassium permanganate, followed by distillation. The sodium chloride was recrystallised, carefully dried, and introduced in a small silvered copper vessel. Measurements were made with mixtures of alcohol and water varying from 0 to 200 molecules of alcohol per 200 molecules of water, and a maximum absorption of heat was found for the solution containing about 33% alcohol. This value coincides approximately with that obtained by Dupré and Page (compare *Phil. Trans.*, 1861, 151, 591) by the maximum heat of solution of alcohol in water. The author considers that his results support the theory of stable hydrates in solution.   W. G.

Heat of Vaporisation of the Metals. ARTHUR WEHNELT and CHR. MUSCELEANU (*Ber. Deut. physikal. Ges.*, 1912, 14, 1032—1034).— A strong current is passed through a discharge tube provided with a platinum cathode coated with calcium oxide and an anode of the metal the heat of vaporisation of which is to be determined. The current strength, anode fall of potential, time during which the current is passed, and the loss in weight of the anode are measured. From these data it is shown that the heat of vaporisation of the anode metal can be calculated. In this way the following values have been obtained : mercury, 63·6 ; cadmium, 181·0 ; zinc, 365·8 ; magnesium, 1700·0, and bismuth, 161·5.   H. M. D.

Free Energy of Organic Compounds. I. Reversible Synthesis of Carbamide and of Ammonium Cyanate. GILBERT N. LEWIS and GEORGE H. BURROWS (*J. Amer. Chem. Soc.*, 1912, 34, 1515—1529).—It is pointed out that a reaction is only possible thermodynamically when the total free energy of the products is less than that of the reacting substances, and that true equilibrium only exists when the difference of free energy between the factors and the products is zero. The free energy affords the only true measure of chemical affinity, and when the free energies of all the substances involved in a reaction are known, it will be possible to predict the direction and extent of the reaction. It is therefore desirable that the free energy of important compounds should be known with direct reference to the elements of which they are composed. In order to obtain the free energy of an organic compound, it is necessary that the compound should be synthesised from its elements by a series of processes in each of which a true equilibrium is investigated. In the present paper, an account is given of a study of the synthesis of carbamide and ammonium cyanate from ammonia, carbon dioxide, and water, the free energy for these three substances having already been determined.

A study of the equilibrium between carbamide, carbon dioxide, ammonia, and water was made by heating aqueous solutions of carbamide in sealed tubes at 132°, 111°, and 77°, and afterwards analysing the contents of the tubes. Similar experiments were made with solutions of ammonium carbamate. The free energy change of

the reaction $2NH_3 + CO_2 = CO(NH_2)_2 + H_2O$ being zero at equilibrium, it follows that if the free energies of ammonia, carbon dioxide, and water in this mixture are known, that of carbamide is also known. It was necessary therefore to determine the relations between the free energies of these substances in the equilibrium mixture and their free energies under normal conditions. This was effected by determining the vapour pressure of water, carbon dioxide, and ammonia above the equilibrium mixture; from the data so obtained the free energy of carbamide in that mixture could be calculated. The activity of carbamide in the equilibrium mixture was then ascertained in relation to that of solid carbamide by determining the distribution of carbamide between the equilibrium mixture and ethyl acetate. From the results obtained it is shown that for $CO_2(gas) + 2NH_3(gas) = CO(NH_2)_2(solid) + H_2O$ (liquid) : $\Delta F = -1772$.

The relative activity of carbamide in the solid state and in dilute aqueous solution was next determined in an indirect way by means of a study of the vapour pressure of water at $25°$ over various aqueous solutions of carbamide, and it was found that for $CO(NH_2)_2(solid) = CO(NH_2)_2(molal) : \Delta F = -1562$. This when combined with the previous equation gives $CO_2(gas) + 2NH_3(gas) = CO(NH_2)_2(molal) + H_2O(liquid) : \Delta F = -3334$.

The equilibrium between carbamide and ammonium cyanate in dilute aqueous solution has been determined by Walker and Hambly (T., 1895, **67**, 746), Walker and Kay (T., 1897, **71**, 507), and Fawsitt (A., 1903, ii, 15). From their results and the value of the heat of the reaction, $CO(NH_2)_2 = NH_4{}^{\cdot} + CNO'$, recorded by Walker (A., 1903, ii, 136), it is found that for $CO(NH_2)_2(molal) = NH_4{}^{\cdot}(molal) + CNO^-(molal) + H_2O(liquid) : \Delta F = 2766$. This constant enables the free energy of formation of hydrogen cyanide to be calculated.

E. G.

New Forms of Whirling Gaseous Combustion and Their Analogy with the Appearance of Certain Astronomical Phenomena. JEAN MEUNIER (*Compt. rend.*, 1912, **155**, 1243—1246). —A further study of the "spiral flame" (compare A., 1912, ii, 432). By increasing the pressure on the gas supplying the wide flame to one-tenth of that supplying the jet, a different result is obtained, the narrow flame being bent back, and new phenomena appear. Diagrams are given showing the result, and a further analogy is drawn between these phenomena and star formation.   W. G.

Polymerisation of Liquids and a General Method for Determining its Relative Value. MADISON M. GARVER (*J. Physical Chem.*, 1912, **16**, 669—678. Compare A., 1912, ii, 830).—The total pressure on a liquid (internal and external) is balanced by a kinetic pressure equal to that the liquid would exert if it were a perfect gas at the same temperature and density. This equilibrium is maintained by reason of the fact that the degree of polymerisation of the liquid is a function of the temperature and density, and thus polymerisation acts as a stabiliser to the system, that is to say, a "source and sink" of heat energy.

If H is the heat of polymerisation per gram of a vapour with molecular weight m, Hm is the heat of polymerisation per gram-molecule and is proportional to n, the number of molecules polymerised per gram-molecule on liquefaction, that is, $Hm = Kn$.   The author assumes that K has the same value for all vapours at the same temperature and writes $H_1 m_1/H_2 m_2 = n_1/n_2$, where m_1 and m_2 are the molecular weights of the vapours of two different substances.   It follows simply that $H_1 m_1/H_2 m_2 = x_2(x_1 - 1)/x_1(x_2 - 1)$, where x_1 and x_2 are the respective polymerisation factors of the two liquids.

Hence, knowing the amount of polymerisation which occurs in any one substance on passing from the gaseous to the liquid state, it is possible to calculate the amount of polymerisation of any other liquid at the same temperature from the relative values of H and m.   If the absolute degree of polymerisation of the liquid is required, the value x must be multiplied by the polymerisation coefficient of the vapour.

The author calculates the values of x for water between $0°$ and $200°$ from the specific volumes, and, using these values, deduces x for thirteen organic liquids at their respective boiling points.   It has already been suggested that the so-called "normal" liquids of Ramsay and Shields are polymerised and the values of x now obtained, ranging between $1 \cdot 40$ and $2 \cdot 48$, confirm this view.   The apparently exceptional behaviour of acetic acid (*loc. cit.*) is shown to have been due to an error in calculation.   R. J. C.

A Thermodynamic Measure of Polymerisation.   MADISON M. GARVER (*J. Physical Chem.*, 1912, 16, 679—681.   Compare A., 1912, ii, 536).—The proof previously given that the degree of tension in a surface film is equal to the intrinsic pressure of the liquid referred to the density in the surface film involved the use of the function ϵ, the range of molecular action in the surface film.

The author's basic equation $\gamma/2\epsilon = \rho RT/m$ is now deduced without any assumption as to the meaning of ϵ, so that it constitutes "a secure foundation upon which to build a thermodynamic theory of the degree of polymerisation of liquid substances."   R. J. C.

The Second Virial Coefficient for Monatomic Gases and for Hydrogen Below the Boyle Point.   W. H. KEESON (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 643—648.   Compare A., 1912, ii, 1138).—Assuming that the potential energy of the attraction between the molecules is proportional to r^{-q}, where r is the distance between the molecular centres and q a constant, the author has examined the behaviour of hydrogen, argon, and helium at low temperatures with the object of deducing the value of the exponent q.   In the case of hydrogen the data agree with $q = 4$.   For argon, the interval of temperature for which data are available is too small to allow of a definite conclusion being reached.   At temperatures below $-100°$, the data for helium indicate also that $q = 4$, although the behaviour of the gas at higher temperatures is not in agreement with this value.

                                                        H. M. D.

Physical Constants of Certain Important Chlorinated Hydrocarbons Used as Solvents. WALTER HERZ and W. RATH-MANN (*Chem. Zeit.*, 1912, 36, 1417—1418).—Measurements have been made of the densities, coefficients of expansion, and vapour pressures of chloroform, carbon tetrachloride, trichloroethylene, tetrachloro-ethylene, *s*-tetrachloroethane, and pentachloroethane at a series of different temperatures. The densities at 25° and the coefficients of ex-pansion are respectively :—chloroform, 1·4791, 0·001257 ; carbon tetra-chloride, 1·5835, 0·001227 ; trichloroethylene, 1·4542, 0·001193 ; tetra-chloroethylene, 1·6080, 0·001078; *s*-tetrachloroethane, 1·5881, 0·000998 ; pentachloroethane, 1·6712, 0·0009097.   From the vapour-pressure data it is apparent that the six substances form a group for which the Ramsay-Young rule is valid, the value of the ratio $T^\circ_{760}/T^\circ_{800}$ being equal to about 1·085.   From the variation of the boiling point with the pressure between pressure limits of about 0·5 and 1 atmosphere, the following molecular heats of vaporisation have been calculated— trichloroethylene 7436 cal., tetrachloroethylene 8554 cal., *s*-tetrachloro-ethane 9134 cal., pentachloroethane 8829 cal.   These values are in agreement with Trouton's rule.   H. M. D.

The Drawing Out of Metals. MAURICE HANRIOT (*Compt. rend.*, 1912, 155, 971—974).—A study of the hardness, breaking strain, and elongation of metals when submitted to drawing-down.   Metals only slightly hardened, although to different degrees, have practically the same breaking strain and elongation.   Drawing out tempers metals much more highly, when they are almost completely annealed, whereas with metals possessing more than a certain degree of hardness it seems to exert a kind of annealing effect.   Tempering by traction, as measured by increase in hardness, only commences after the metal has undergone a permanent deformation.   W. G.

Viscosity Law for Liquids. ALEXIUS J. BATSCHINSKI (*Physikal. Zeitsch*, 1912, 13, 1157).—If the specific volumes of a non-associated liquid at a series of different temperatures are plotted with reference to the fluidities at the corresponding temperatures, it is found that the points obtained lie very nearly on a straight line.   From this relation-ship the author draws the conclusion that the viscosity of a liquid is determined by the specific volume.   H. M. D.

Effect of the Transition Layer of a Liquid on its Surface Tension. RICHARD D. KLEEMAN (*Phil. Mag.*, 1912, [vi], 24, 876—885). —It is shown that the formation of a transition layer at the surface of a liquid, in which the distribution of the molecules is different from that in the interior of the liquid, has the effect of decreasing the magnitude of the surface tension.   A formula is deduced from which the value of the surface tension may be calculated for the case where no transition layer is formed.   This is applied to the data for ethyl ether, carbon tetrachloride, methyl formate, and benzene.   The surface tension values thus obtained are nearly twice as large as the experi-mentally determined surface tensions.   Since the differences represent the external work done in the formation of the transition layer, it is

evident that the influence of the formation of the transition layer on the surface tension is very considerable. This influence is approximately independent of the temperature.

The formula referred to above may also be applied to liquid mixtures. In this case the difference between the calculated and observed surface tensions represents the external work during the formation of the transition layer, and in altering the relative proportion of the constituents.　　　　　　　　　　　　　　　　　　　H. M. D.

The Laws of Surface Adsorption and the Potential of Molecular Attraction. J. R. KATZ (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 445—454).—The adsorption of water by finely divided quartz and anorthite has been examined. Weighed quantities of these substances, both obtained synthetically, were left for several days in contact with air exposed to the action of a 1% solution of sulphuric acid. The substances were then placed over mixtures of sulphuric acid and water of known vapour pressure until the weight had become constant. The loss of weight on ignition then gave the quantity of water adsorbed.

If the quantity of adsorbed water is marked off as abscissa and the relative vapour pressure p/p_0, where p_0 refers to pure water, as ordinate, characteristic curves are obtained. The first part of the curve is nearly horizontal, but when the adsorption reaches a certain value it rises very quickly and again becomes approximately horizontal.

This form of curve is supposed to be connected with the variation of the vapour pressure with the thickness of the water film on the surface of the solid. When the formula, $RT \ln p/p_0 = k$, which connects the vapour pressure p with the molecular attraction k is applied to the adsorption data, it is found that the attraction potential diminishes rapidly with increasing thickness of the film, but that there is a fairly well-defined radius of attraction, which in the case of water on the quartz surface amounts to 1.3×10^{-6} cm., and on the anorthite surface to 6.2×10^{-6} cm.　　　　　　　　　　　　　　H. M. D.

Adsorption by Clays. IV. PAUL ROHLAND (*Biochem. Zeitsch.*, 1912, 46, 374—375).—The colouring matter of waters from sulphite cellulose factories is not adsorbable by clays unless treated with potassium ferrocyanide, when the pigment is converted into Prussian-blue.　　　　　　　　　　　　　　　　　　　　S. B. S.

Thermal Dissociation and Constitution of Readily Decomposable Salts. K. FRIEDRICH (*Centr. Min.*, 1912, 174—184, 207—220).—An electrical apparatus is described in which the tem-

Decomposition				Decomposition		
of	into	commenc-ing at		of	into	commenc-ing at
$Fe_2(SO_4)_3$	Fe_2O_3	705°		$3ZnSO_4$	$3ZnO,2SO_3$	840 ca.
$CoSO_4$	CoO	880		$3ZnO,2SO_3$	$3ZnO$	935
$NiSO_4$	NiO	840		$MnSO_4$	?	1030
$2CuSO_4$	$2CuO,SO_3$	740		$Al_2(SO_4)_3$	Al_2O_3	770
$2CuO,SO_3$	$2CuO$	845		Ag_2SO_4	$2Ag$	1085
$4CuO$	$2Cu_2O$	1040 ca.				

perature of a substance can be gradually raised, during sixty minutes, up to 1350°. The temperatures are plotted against time, and heating (and heating-velocity) curves are given. The results obtained at atmospheric pressure and in a still atmosphere are shown on page 27.

$MnSO_4$ has m. p. 700°; transformation point 860°. Ag_2SO_4 has m. p. 660°; transformation point 410°. $ZnSO_4$ and $PbSO_4$ have the transformation points 740° and 850° (approx.) respectively.

<div align="right">L. J. S.</div>

Thermal Dissociation and Constitution of Readily Decomposable Minerals. K. FRIEDRICH and L. GARRETT SMITH (*Centr. Min.*, 1912, 616—626, 651—660, 684—693).—Various mineral carbonates were heated gradually during one hour up to 1130°, and the heating (and heating-velocity) curves plotted. The results obtained at atmospheric pressure and in a still atmosphere are tabulated below :

Substance.	Commencing decomposition.	Maximum decomposition.
Cerussite from Mies, Bohemia	about 815°	335°
Calamine from Thasos, Turkey	395	440
Chalybite from Ivigtut, Greenland	⎱ ca. 400 ?	460
,, ,,, Neudorf, Harz	⎰	480
,, ,, Niederschelden, Westphalia		500
Rhodochrosite from Colorado	525	570
,, ,, Peru	510 ?	550
Magnesite from Kaiserberg, Styria	570	600
Calcite from Löwenberg, Silesia	895	910
Aragonite from Bilin, Bohemia	895	910
Strontianite from Hamm, Westphalia	over 1130	—
Witherite (locality ?)	,, 1130	—

In all cases, except for cerussite, strontianite, and witherite, the decomposition into oxide and carbon dioxide is complete. Cerussite alters into a basic carbonate at about 315—335°, and this is decomposed into lead oxide and carbon dioxide at 430—460°. Strontianite and witherite show an absorption of heat, corresponding with a transformation at 830—860° and 780—815° respectively.

In addition to these simple carbonates, various double carbonates (dolomite, ankerite, etc.) were also examined, and heating curves are given. Analyses are given for each mineral examined.

<div align="right">L. J. S.</div>

Mechanism of Osmosis. ALF. GILLET (*Bull. Soc. chim. Belg.*, 1912, 26, 502—503).—A mathematical amplification of some points discussed in a previous paper (A., 1912, ii, 1043). H. W.

The Kinetic Theory of the Osmotic Pressure of Concentrated Solutions, and the Agreement of Henry's Law for Concentrated Solutions of Carbon Dioxide in Organic Solvents at Low Temperatures. OTTO STERN (*Zeitsch. physikal. Chem.*, 1912, 81, 441—476).—The author deduces an expression, which shall represent the osmotic pressure of concentrated solutions, from theoretical considerations based on the van der Waals gas equation. The discussion of the formula leads to the conclusion than a given

substance will obey the osmotic laws much better than the same substance obeys the gas laws when it is in the gaseous condition. The second part of the paper is concerned with the experimental investigation of the formula deduced in the first part. This consists in examining solutions of carbon dioxide in ethyl alcohol, methyl alcohol, acetone, ethyl acetate, and methyl acetate at temperatures of $-78°$ and $-59°$, and at pressures from 50 mm. to 760 mm. of mercury. The experimental results show that Henry's law holds very exactly for concentrated solutions when expressed in terms of "solubility" (Ostwald), whereas in terms of the absorption coefficient (Bunsen) it does not hold. The osmotic pressure, calculated from the measurements, is in good agreement with that calculated from the theoretical formula deduced in the first part of the paper. The last portion of the paper consists of a consideration of Dolezalek's "Theory of Gaseous Solubility" (A., 1910, ii, 184) in connexion with the results obtained by the author. It is shown that the explanation given by Dolezalek for irregularities leads to results which are entirely opposed to those generally accepted.

J. F. S.

Activity of the Ions and the Degree of Dissociation of Strong Electrolytes. GILBERT N. LEWIS (*J. Amer. Chem. Soc.*, 1912, 34, 1631—1644).—A review is given of the facts hitherto published bearing on the question of the degree of dissociation of electrolytes, and their probable theoretical significance is discussed. Attention is directed more particularly to the properties of strong uni-univalent electrolytes, as these afford the only data from which conclusions, free from ambiguity, can be drawn.

It is shown that many chlorides, bromides, and iodides are equally dissociated, whilst nitrates, chlorates, bromates, and salts of silver and thallium are somewhat less dissociated. The degree of dissociation of uni-univalent salts is probably much less than is usually supposed. If it is assumed that potassium chloride is dissociated to the extent of 74% at $0.1M$, 82% at $0.05M$, and 89% at $0.02M$, then in most cases up to $0.1M$ the activity of the ions is proportional to the concentration of the solution.

According to this view, the deviation of strong electrolytes from the mass law is to be attributed largely to a general increase in ionic mobility with the total ion concentration. This is in agreement with Jahn's theory (A., 1900, ii, 523), but differs from that advanced by Franklin and Kraus (A., 1905, ii, 298) and Lewis and Wheeler (A., 1906, ii, 650). According to the former explanation, it is the velocity of the ions which fails to obey the laws of the ionic theory, whilst, according to the latter, it is the degree of dissociation. Probably neither explanation is adequate by itself, but the evidence now adduced in support of the view that the ions in aqueous solution have a variable mobility renders further investigation desirable.   E. G.

Neutralisation Curves and Dissociation Constants of Sulphuric and Citric Acids. JOHANNES E. ENKLAAR (*Zeitsch physikal. Chem.*, 1912, 81, 481—482).—Polemical. An answer to the criticism of Drucker (A., 1911, ii, 687) on Enklaar's papers (A., 1911, ii, 1071; 1912, ii, 239).   J. F. S.

The Absorption of Oxygen, Nitrogen, and Hydrogen in Aqueous Solutions of Non-electrolytes. CARL MÜLLER (*Zeitsch. physikal. Chem.*, 1912, 81, 483—503).—The solubility of oxygen, nitrogen, and hydrogen is determined in aqueous solutions of sucrose, dextrose, glycerol, and chloral hydrate which vary in concentration from 10% to 60%. In the glycerol and chloral hydrate solutions the absorption coefficient decreases to a minimum and then increases with increasing concentration of the solutions, whilst in the sucrose and dextrose solutions the absorption coefficient increases steadily with increasing concentration. Tho relative decrease in the absorption coefficient at a given concentration of the solution is independent of the nature of the gas in the cases examined. The amount of gas absorbed can be represented hy two straight lines which cut at the point of minimum absorption. The minimum ahsorption ie found, for all the gasee investigated, to lie at about the same concentration. The fact that the decrease of the absorption coefficient is independent of the nature of the gas can only be explained hy the formation of hydrates in the solutions, and consequently it is to he regarded ae a proof of the existence of hydratee in eolutions.   J. F. S.

Liquid Mixtures. I. Property-composition Curves and the Molecular Changes which take Place on Forming Binary Liquid Mixtures. ROBERT B. DENISON (*Trans. Faraday Soc.*, 1912, 8, 20—34).—The existence of a chemical compound may be inferred with probability, but not with certainity, from the presence of a maximum or minimum in the property-composition curve. The deviation from a straight line is a maximum for the composition corresponding with that of the compound. This is independent of the dissociation of the compound. An approximate eetimate of the extent of dissociation is obtained hy examining the deviation-composition cnrve, a sharp maximum denoting a small dissociation. Changes of temperature may displace a maximum on the property-composition curve, hut do not alter the position of the maximum on the deviation curve. It is thue possible to determine the equilibrium in a homogeneous solution hy determining any euitable physical property of a series of binary mixtures.
     C. H. D.

Liquid Mixtures. II. Chemical Combination in Liquid Binary Mixtures as Determined by a Study of Property-composition Curves. ROBERT B. DENISON (*Trans. Faraday Soc.*, 1912, 8, 35—50).—The principles discussed in the preceding abstract are applied to several cases of contraction on mixing, and of the viscosity of liquid hinary mixturee. The curves for mixtures of ethyl alcohol and water show a maximum deviation at 46% alcohol, corresponding with a compound $EtOH,3H_2O$. The position of the maximum is the same at $0°$ and $15·6°$, hut the maximum is sharper at the lower temperature, indicating dissociation as the temperature rieee. The pyridine–water curves indicate in similar manner a compound $C_5NH_5,2H_2O$, whilst mixtures of lactic acid with water and of acetic acid with benzene, indicate compounds $C_3H_6O_3,2H_2O$,

and $C_6H_6,2C_2H_4O_2$ respectively.   The method is also applied to aqueous solutions of salts, and a theoretical discussion follows.

C. H. D.

Systematics of the States of Aggregation of Matter.
P. P. von Weimarn (*Koll. Chem. Beihefte*, 1912, 4, 65—100).—A further discussion of the author's orientation theory (compare A., 1910, ii, 1048; 1912, ii, 142, and other papers). The views of Lehmann are adversely criticised, and arguments advanced against the assumption of the amorphous state.   H. M. D.

The Nature of Pseudo-solutions. Basil Kurilov (*Zeitsch. anorg. Chem.*, 1912, 79, 88—96. Compare A., 1906, ii, 343).—The system studied is that of ferric hydroxide hydrosol and hydrochloric acid.   The transition from pseudo-solution to true solution is observed in this system, the quantity of precipitate reaching a maximum for a certain concentration of the acid. The solid phase also alters in character as the change proceeds.   Measurements of the optical extinction coefficient give the same result.   The conclusion is confirmed, that the formation of a pseudo-solution depends on the formation of additive compounds.   C. H. D.

The Theory of the Isoelectric Point. III. The Nature of Solutions of Colloids of the Character of Proteins. Leonor Michaelis (*Biochem. Zeitsch.*, 1912, 47, 250—259. Compare A., 1911, ii, 192, 577).—Sörensen has recently criticised the author's theory that the optimal condition for precipitation of substances from solution exists when the solution is isoelectric with the dissolved substance (*Ergebnisse der Physiologie*, 1912, 506).   The author gives reasons for maintaining his position.   He shows incidentally that the isoelectric points of phenylalanine and glycine, ascertained by determining the mixture of sodium acetate and acetic acid to which their concentrated aqueous solutions can be added without alteration of the hydrogen-ion concentration, agree accurately with isoelectric points calculated from their basic and acidic dissociation constants.   He also calls attention to the fact that the peculiar properties of the protein colloidal solutions, as contrasted with those of amphoteric, slightly soluble crystalline substances, can be explained by the differences of the surface tensions of the interfaces, the surface tension in the case of crystalline substance and its saturated solution being great, whereas in the case of the protein colloids it is small.   This last factor tends to cause dispersion of the colloid in solution, and to inhibit the tendency to crystallisation, which latter phenomenon, in the case of crystalline substances, is promoted also by the vectorial forces.   S. B. S.

Theory of the Formation and Stability of Colloidal Solutions and Precipitates. II. P. P. von Weimarn (*Koll. Chem. Beihefte*, 1912, 4, 101—131. Compare A., 1910, ii, 835).—The theory of the so-called condensation methods for the production of disperse systems is further discussed.

Experiments are described which show the gradual change in the

character of precipitated sodium chloride when the conditions (nature of the solvent, temperature) under which the precipitation is effected are gradually altered. These structural changes are illustrated by photographs of the precipitated substance. Similar variations in structural character have been observed in the case of a large number of other substances.   H. M. D.

Formation of New Colloids in a Colloidal Solution by Metallic Plates. MAURICE PHILIPPSON (*Bull. Acad. roy. Belg.*, 1912, 580—582. Compare A., 1912, ii, 914).—Colloidal copper, when prepared by Bredig's method, gradually undergoes a change when carefully cleansed plates of either zinc or platinum are introduced into the solution of the hydrosol. A study of Tyndall's phenomenon in these solutions shows that, whilst the copper is gradually precipitated, a new and not very stable colloid is produced. Contrary to the explanation previously put forward (*loc. cit.*), the precipitation is independent of the electrolytic solution pressures of the precipitating metals, and these metals, under the influence of the discharge of the colloidal particles during precipitation, are able in their turn to assume the colloidal state.   W. G.

The Emulsoid Condition and the General Classification of Colloidal Forms. WOLFGANG OSTWALD (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 230—239).—The classification of colloidal forms of matter is discussed with special reference to the emulsoid condition. According to the author, emulsoid and lyophilic are not synonymous terms, the lyophilic colloids representing merely a special group of emulsoids. Since the term lyophilic is employed in reference to colloids in which the dispersive medium is combined to a greater or smaller extent with the disperse phase, it is suggested that such colloids may more conveniently be called solvated, the lyophobic colloids being then designated non-solvated.

As a direct test for the emulsoid condition, the formation of two distinct non-disperse liquid layers on coagulation is recommended. This type of coagulation has been observed in the case of gelatin, casein, soaps, lipoids, and silicic acid.   ·   H. M. D.

Jellies. P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 239—241).—Polemical against Zsigmondy and Bachmann (A., 1912, ii, 1149). The crystalline character of the ultra-microscopic particles exhibited by certain jellies had been previously demonstrated by the author.   H. M. D.

Maximum and Minimum Equilibrium Pressure in Binary Systems. F. E. C. SCHEFFER (*Zeitsch. physikal. Chem.*, 1912, 81, 431—440).—A theoretical paper dealing with the conditions under which maximum and minimum pressures occur in $L + G$ and $S + G$ and $S + L$ surfaces. The work is a continuation of that of Smits (A., 1912, ii, 242). The author concludes, from theoretical considerations, that the systems $HgI_2 + HgBr_2$, $d + l$ carvoxime, monochloro- and mono-bromo-quinol acetates, p-azoxyphenetole + p-methoxycinnamic acid,

and many binary metal systems ought to show curves of maximum and minimum pressure on the *SL* surface. 　　　　　　　J. F. S.

Examples of Bimolecular Reversible Reactions. WALTER HERZ and FRITZ KUNTZE (*Zeitsch. Elektrochem.*, 1912, **18**, 1015--1016). --A theoretical paper in which equilibrium constants are calculated from experimental results of F. Kuntze on the reaction between chloral alcoholates and alcohols (compare A., 1908, i, 322). The following constants are given : chloral-amyl alcoholate + ethyl alcohol, $k_1/k =$ 0·444 ; chloral-amyl alcoholate + propyl alcohol, 0·444 ; chloral propyl alcoholate + *l*-amyl alcohol, 0·121 ; chloral butyl alcoholate + *l*-amyl alcohol, 0·121 ; chloral amyl alcoholate + benzyl alcohol, 0·298.
　　　　　　　　　　　　　　　　　　　　　　　　　J. F. S.

Gaseous Mineralisers in a Magma. II. PAUL NIGGLI (*Zeitsch. anorg. Chem.*, 1912, **77**, 321—334. Compare A., 1912, ii, 632).--A further theoretical discussion of ternary systems including a gaseous phase. 　　　　　　　　　　　　　　　　　　　　　　C. H. D.

Equilibria in Quaternary Systems. V. Completely Isomorphous Quaternary Mixtures. NICOLA PARRAVANO (*Gazzetta*, 1912, **42**, ii, 305—326).—The study of the phenomena of crystallisation of quaternary systems by the tetrahedral method of representation (compare A., 1911, ii, 973) involves the erection, at the angles of the tetrahedron, of ordinates in space of four dimensions. The author treats the problem mathematically, and shows how it is possible to obtain the results required in spite of the impossibility of drawing such ordinates. Four typical cases present themselves and these are considered in turn. 　　　　　　　　　　T. H. P.

Distribution of Dyes between Two Solvents. The Theory of Dyeing. WILLEM REINDERS and D. LELY, jun. (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 482—495).—The influence of concentration on the distribution of a number of dyes between *iso*butyl alcohol and water has been examined. Denoting the corresponding concentrations in the alcohol and water by c_a and c_w respectively, it is found that the ratio c_a/c_w decreases in all cases as the concentration increases. For some dyes, the observations can be satisfactorily represented by means of the adsorption formula : $\log c_a = 1/n \log c_w$, but for others this is by no means the case, and in order to obtain approximate agreement between the calculated and observed values, it is necessary to assume larger values of $1/n$ for the more concentrated solutions. For the dyes examined, the value of $1/n$ varies from 0·3 for erythrosine-*A* to 1·0 for alkali-blue and crystal ponceau.

The increase of $1/n$ with the concentration may be explained on the assumption that the absorption of the dye by the alcohol is mainly dependent on the concentration of the non-ionised and hydrolytically dissociated molecules.

This view accords with the fact, that in the case of basic dyes, the transition from the water to the alcohol layer is increased by the addition of bases, whilst in the case of acid dyes the addition of acids has a similar effect. This influence of acids and bases has been

examined in the case of acid, basic and substantive dyes, and the observed changes in distribution, together with the accompanying change in colour, are recorded in each case.

When the facts relating to the distribution of dyes between water and *iso*butyl alcohol and between water and fibrous substances are compared, there can be no doubt that a close similarity exists, and the authors conclude that the absorption of dyes by fibres is essentially dependent on the formation of solid solutions. The assumption of a surface adsorption is in many cases quite unnecessary.

H. M. D.

The Calculation of Equilibrium Constants from Cryoscopic Measurements. J. B. GOEBEL (*Zeitsch. physikal. Chem.*, 1912, 81, 298—307).—A continuation of the work described in previous papers (compare A., 1910, ii, 268; 1911, ii, 1078). The present paper deals with the calculation of the dissociation and association constants of binary electrolytes and with the first and second dissociation constants of ternary electrolytes. The results show that, in general, these electrolytes follow the law of mass action. Equations are given for the calculation of the conductivity of ternary electrolytes. A number of printer's errors in the previous papers (*loc. cit.*) are corrected. For the deduction of the numerous equations, the original paper must be consulted. Among the general conclusions arrived at, the following may be noted : (1) The weak organic acids are all polymerised to about the same extent in aqueous solution, and have, approximately, the same polymerisation constant, 0·5 ; (2) of salts in aqueous solution the sulphates are the most strongly polymerised, the nitrates somewhat less, and the chlorides least of all ; (3) generally the weaker the electrolyte, so far as salts are concerned, the more strongly is it polymerised ; (4) the potassium salts are more strongly polymerised than the corresponding sodium salts.   J. F. S.

[Reciprocal Salt Pairs.] OTTO MENGE (*Zeitsch. physikal. Chem.*, 1912, 81, 377—378).—A reply to criticisms made by Jänecke (A., 1912, ii, 762) on a previous paper of the authors (A., 1911, ii, 982).   J. F. S.

Theory of the Efflorescence of Saline Hydrates. CH. BOULANGER and GEORGES URBAIN (*Compt. rend.*, 1912, 155, 1246—1249).—For the efflorescence of salts in a dry atmosphere the authors deduce the equation $\log (m_\theta - m_t) = \log a + A \log(\theta - t)$, where θ is the total time necessary for efflorescence, m_θ the corresponding loss in weight, and m_t the loss at any given time t. a and A are constants, the value of the latter being 1·6 for most hydrates. Results are given for sodium sulphate, $Na_2SO_4,10H_2O$, and the values obtained experimentally are in close accord with those calculated. This agreement is less satisfactory in the case of salts which in the anhydrous form retain traces of water except at high temperatures.   W. G.

Saturation of the Ethylenic Bonds of Oleic Acid by means of Iodine and the Molecular Weight of Dissolved Iodine. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1912, [iv], 11, 1006—1009. Compare A., 1911, ii, 266).—The author has measured the velocity of

the addition of iodine to oleic acid in carbon tetrachloride and in ethyl acetate solution at different dilutions. In each case, the reaction is found to be bimolecular, and the molecule of dissolved iodine thus appears to be diatomic. The difference in colour of the two solutions is attributed to the probable existence of free molecules of iodine in carbon tetrachloride solution and to a combination of iodine with ethyl acetate when dissolved in the latter solvent. H. W.

Hydrolysis of Metallic Alkyl Sulphates. GEORGE A. LINHART (*Amer. J. Sci.*, 1912, [iv], 34, 539—542).—The velocity of hydrolysis of calcium and strontium ethyl sulphate under the catalytic influence of hydrochloric acid has been measured at 60° in order to ascertain the influence of the replacement of barium in barium ethyl sulphate (A., 1912, ii, 927) by calcium and strontium. The rate of decomposition of the salts decreases as the weight of the metal decreases, the values of the velocity coefficient for N-hydrochloric acid being 0·0083, 0·0078, and 0·0073 for the barium, strontium, and calcium salts respectively. T. S. P.

The Alkaline Decomposition of Chlorohydrins. L. SMITH (*Zeitsch. physikal. Chem.*, 1912, 81, 339—376).—The rate of decomposition of neutral and acid chlorohydrins by means of alkalis, both with and without the addition of neutral salts, is investigated in the present paper (compare Evans, A., 1891, ii, 796, and Senter, A., 1910, ii, 276). The following neutral chlorohydrins were used: ethylene chlorohydrin, α-monochlorohydrin, propylene chlorohydrin, *iso*butylene chlorohydrin, β-methyl-Δ²-butylene chlorohydrin, α-dichlorohydrin, and epichlorohydrin. In all cases it is shown that the influence of the different alkalis is the same. The author was unable to prove the presence of glycerol in the product of the reaction with monochlorohydrin and alkali, which was stated by Senter (*loc. cit.*) to be formed. It is shown in the case of α-chlorohydrin that the results are more in accord with a termolecular reaction than with a bimolecular change. The addition of neutral salts has a slight effect on the velocity of the reaction, which, however, is too small to be attributed to a metallic ion catalysis. In the reaction between baryta and epichlorohydrin the case is somewhat different, for here an addition of barium chloride causes an increase in the rate of the reaction, which is larger the smaller the concentration of the hydroxyl ion present. The following chlorohydrins of acids were investigated: chloromalic acid, β-chloro-lactic acid, and α-chloro-β-phenyl-β-lactic acid. The reactions were studied with sodium hydroxide, potassium hydroxide, baryta, and calcium hydroxide, and in all cases are shown to be bimolecular; there is, however, a catalytic influence exerted on the velocity of the reactions by the metallic ions present. The Holmberg constant, d (see Holmberg, A., 1912, ii, 443, 1048), and the catalysis constant for chloromalic acid with different bases are as under:

	Ca(OH)₂.	Ba(OH)₂.	KOH.	NaOH.
Catalysis const.	55	42·9	11·4	10·6
d..	1/12	1/3	1/4	1/4

With β-chlorolactic acid the values are:

	Ca(OH)$_2$.	Ba(OH)$_2$.	KOH.	NaOH.
Catalysis const.	3·8	1·79	0·74	0·74
d	1/4	1/4	1/7	1/7

Similar results are also given for α-chloro-β-phenyl-β-lactic acid, in connexion with which the existence of two isomerides is shown, m. p. respectively 94° and 103°.   J. F. S.

Inorganic Ferments. VI. Catalytic Decomposition of Formic Acid by Rhodium. THOMAS BLACKADDER (*Zeitsch. physikal. Chem.*, 1912, 81, 385—416. Compare Bredig and co-workers, A., 1900, ii, 213; 1901, ii, 441, 442; 1909, ii, 389; 1910, ii, 284). —The velocity of the decomposition of formic acid by means of rhodium has been investigated by the author, together with the influence of changes in the various conditions of carrying out the decomposition. The most active rhodium is produced by allowing rhodium sponge to lie in contact with potassium sulphide for several hours, or by electrolytically depositing rhodium black on to platinised platinum from a solution of rhodium in 60% sulphuric acid by a current of 0·02 ampere at 180°. Rhodium is only capable of effecting the catalysis when it contains either sulphur or oxygen. In the latter case, the activity is of short duration, whilst in the former case it persists for several days. Formic acid is practically quantitatively decomposed into hydrogen and carbon dioxide, and a small amount of hydrogen sulphide, amounting to 0·02%, is evolved at the same time. The reaction is complicated, as shown by the constant, which, when calculated from the equation for reactions of the first order, increases with decrease of the formic acid concentration. The temperature-coefficient of the reaction between 85° and 95° is rather more than 2 per 10° rise of temperature. The effect of more rapid stirring is slight, and this, taken in conjunction with the temperature-coefficient, indicates that the process is to a large extent purely chemical and does not depend on diffusion. The addition of sodium formate increases the velocity of the reaction, whilst the addition of sufficient alkali to make the solution alkaline entirely stops the reaction. Dilution of the formic acid and sodium formate mixture brings about an increase in the velocity of the change. The addition of hydrochloric acid decreases the velocity of the reaction, which indicates that the increase brought about by sodium formate is due to a decrease in the concentration of the hydrogen ions. Active rhodium has a more positive potential than inactive rhodium when measured in formic acid solution.
     J. F. S.

Catalysis on the Basis of Work with the Imino-esters: the "Salt Effect" JULIUS STIEGLITZ (*J. Amer. Chem. Soc.*, 1912, 34, 1687—1695).—Investigations of the action of ammonia on imino-esters (A., 1908, ii, 168) indicated that, in addition to the reaction of the anion of the imino-ester with a high velocity coefficient, a second accelerating force is involved, the imino-ester itself exerting a "salt effect" on its own catalysis. In more recent work on the velocity of

the rearrangement of acid chloroamides through salt and ion formation in alkaline solutions, it has been found that not only do the anions of the salts formed undergo the rearrangement, hut that possibly both the anions and the non-ionised salts suffer the rearrangement simultaneously, and that probahly the anions are the rapidly reacting components.

In view of these results, the work on the decomposition of imino-esters hy water has heen re-investigated in order to ascertain whether a parallel action of water on the non-ionised imino-ester, proceeding simultaneously with the main action on tho imino-ester ion, could be inferred. In referring the velocity of the action to the iou as the sole reacting component of the imino-ester, it was necessary to assume a considerahle acceleration of the action in the more concentrated salt solutions, analogous to the "salt effect" in other catalytic actions. The effect of adding neutral salts was generally found to be in harmony with the assumptions made.

Acree has advanced the theory that the accelerations beyond the theoretical effect of a catalyst could he due to a parallel decomposition of ions and non-ionised molecules, and that accelerations occur in which the reacting components are salt molecules and not their ions.

It is shown that the numerical data ohtained in some of the author's experiments agree as well with the hypothesis of a parallel decomposition of the non-ionised salt molecules by water as with the assumption of a "salt catalysis." Further work is therefore being undertaken with a view to determining the salt factor for other reactions in which water is involved.   E. G.

The Natural System of the Elements. A. KLEINER (*Ann. Physik*, 1912, [iv], 39, 1070).—A claim of priority in respect of certain views expressed by Laemmel (A., 1912, ii, 1048) in reference to the influence of temperature on the specific heats of the elements.
                                                                        H. M. D.

The Theory of Radicles as an Interpretation of Mendeleév's System. DAN RADULESCU (*Chem. Zentr.*, 1912, ii, 1418—1420; from *Bul. Soc. Stiinte Bucaresti*, 1912, 21, 59—71).—The structure of an element is considered to be somewhat similar to that of organic compounds; it is built up of a characteristic radicle, the "characteristic" and an indifferent carrier, the "nucleus." The characteristic is the bearer of the valency, the specific and unalterable analytical properties of the element and of the colour, and its weight does not exceed nine times the atomic weight of hydrogen. The nuclei are whole multiples of the three radicles, $R = 22$, $R' = 21 \cdot 27$, and $R'' = 22 \cdot 27$; metallic nature increases from R to R''. Nuclei that approach $10R$ ate radioactive; greater than these are unknown. The characteristics are attached to the nuclei like the various groups to the carbon skeletons in organic compounds. They are seven in number and are equal to: 1 for alkali metals (basic, univalent, coloured flames, few spectral lines, colourless salts); $2 \cdot 07$ for the magnesium group (weak bases, stable salts, bivalent, affinity for carbon); 4 for

characteristics of stable quadrivalence; 5 for tervalence and boron; 8 for sexavalence (blue, green, and red salts, polyammino-compounds and complexes); 7 for quinquivalence, and 5·48 for halogens and manganese. A periodic table shows that from the "constitutional formulæ" based on these theories, the important properties of the elements are made apparent, and that the calculated atomic weights agree very closely with the experimental data.   J. C. W.

Some Considerations Regarding Werner's Theory. ITALO BELLUCCI (*Gazzetta*, 1912, **42**, ii, 532—539).—The author discusses the views of Briggs (T., 1908, **93**, 1564; 1911, **99**, 1019) in regard to the nature of the linking of the ionisable radicles in complex compounds. He is of opinion that the experimental evidence is quite insufficient to justify this modification of Werner's theory, and in particular he points out that Briggs' hypothesis would require the existence of enormous numbers of isomerides among complex compounds, whereas Briggs adduces only a few instances, and in the author's opinion even these require further investigation.   R. V. S.

Laboratory Apparatus. ERNST BERLIN (*Chem. Zentr.*, 1912, ii, 889; from *Zentr. Physiol.*, 1912, **26**, 219—222).—Two pieces of apparatus are figured and described. The first is for use in the preparation of hydrogen chloride by adding sulphuric acid to hydrochloric acid. The second provides for the automatic extraction of substances from one liquid by means of a heavier liquid, for example, extraction of substances from an aqueous solution by means of chloroform.

T. A. H.

Lecture Experiment on the Explosion [and Production] of Electrolytic Gas by Alternating Currents. FRITZ FICHTER (*Zeitsch. Elektrochem.*, 1912, **18**, 1080).—The experiment is designed to show that both products of electrolysis are liberated at a single electrode by an alternating current, and that a large production of gas at an electrode is only possible with large current density when using alternating current. The experiment also demonstrates the explosion of electrolytic gas in a perfectly safe manner. The apparatus consists of a short length of thick-walled glass-tubing, 8 cm. long and 2 cm. diameter; this is fitted with a rubber stopper, which supports a glass stopcock and a platinum wire. The wire serves as one electrode, and projects 3—4 cm. into the tube. The whole is attached to a wooden rod and placed in a beaker of dilute sulphuric acid, so that the tube is filled with the liquid. The tap is then closed. The other electrode consists of a large piece of gas carbon. A current of 7 amperes is passed through, which rapidly fills the tube with electrolytic gas and consequently drives out the solution. Just before the solution has finally left the platinum wire the current density on the wire is great enough to produce a glowing layer of gas which fires the mixture, and allows the tube to refill with solution. The process then repeats itself.   J. F. S.

Photochemistry. IV. Photochemical Lecture Experiments. OSKAR BAUDISCH and ROSE FÜRST (*Ber.*, 1912, **45**, 3426—3428).— The explanation given in a previous paper (A., 1911, ii, 952) of the

formation of α-hydroxyazonaphthalene from ammonium α-nitroso-naphthylhydroxylamine has been confirmed by extracting the yellow dye from the fibre. It was identified as α-azoxynaphthalene, and the methyl-alcoholic solution, on exposure to sunlight, deposited glistening, brownish-red needles of α-hydroxyazonaphthalene.

If filter paper is treated with ammonium α-nitrosonaphthylhydroxyl-amine so as to obtain the yellow dye, and then exposed to the rays from a quartz-mercury lamp, it is turned red, whether screens of glass, glass coated with gelatin, starch solution, or egg-albumin solution, are interposed or not. Such screens, however, prevent the liberation of iodine on paper treated with potassium nitrate and starch iodide, showing that it is the long rays which are active in the first case, and the short rays in the second. The fact that these long rays will penetrate colloidal solutions is discussed in connexion with the utilisation of light energy by the colloidal plasma of plant cells.

By acidifying an aqueous solution of ammonium α-nitrosonaphthyl-hydroxylamine with metaphosphoric acid, an almost white, curdy precipitate of the *free acid* is obtained; white needles from light petroleum, m. p. 54—55°. In chloroform solution the free acid is reduced to α-naphthalenediazonium chloride.　　　　　T. S. P.

Inorganic Chemistry.

The Behaviour of Water as a Liquid and in Five & Modifications Under Pressure. P. W. BRIDGMAN (*Zeitsch. anorg. Chem.*, 1912, 77, 377—455).—The behaviour of water has been examined under higher pressures than in previous experiments, liquid water being studied between −20° and +80° up to 12,000 kilograms per sq. cm., and solid water between −80° and +78° up to 20,500 kilograms per sq. cm. Two new modifications of ice, one of which is capable of existing above 0°, have been discovered. Five of the six stable triple points have been found, and ten of the eleven trans-formation lines have been followed. In addition to the five stable solid modifications, two exist which have no range of stability. All, with the exception of ordinary ice, are denser than water.

The temperature of maximum density of water is independent of the pressure, but the maximum disappears at high pressures ; a new anomaly appears, however, between −15° and −20° at a pressure of 5000 kilo-grams. The increased compressibility at high pressures suggests a possible compressibility of the atoms as well as of the molecules, but the data are still insufficient to construct an equation for the behaviour of liquid water.

The results with the solid phases confirm and extend those of Tammann. The equilibrium curve between ice II and III, which was not found by Tammann, has now been determined. The water is

enclosed in a vessel filled with light petroleum, and the pressure is measured by the change in resistance of a manganin wire.   In order to determine the curve II—III, along which the volume changes are very small, a different method has to be adopted, the temperature being varied at constant volume, and the changes of pressure observed.

Ice VI, which is formed at temperatures above $0°$ under high pressure, has the greatest range of existence, as regards both temperature and pressure, and the form of the curve is such as to indicate that further modifications are not formed.   The existence of two modifications having no range of stability is inferred from the occurrence of volume changes which do not lie on any of the equilibrium curves.

The observations confirm the impossibility of superheating a solid phase with respect to the liquid, whilst undercooling readily takes place, and many of the curves have been prolonged into the region of instability, but an unstable triple point has not yet been realised, and indications of a metastable limit have not been found. Nuclei of a previously existing phase appear to persist even in a solid phase. The velocity of transformation, even in solid phases, is extremely high in the neighbourhood of a triple point, but diminishes rapidly with falling temperature.   The bearing of these results on the theory of the solid state is discussed.   C. H. D.

A New Modification of Sulphur. A. H. W. ATEN (*Proc. K. Wetensch. Amsterdam*, 1912, **15**, 572—583; *Zeitsch. physikal. Chem.*, 1912, **81**, 257—280).—If a solution of rhombic sulphur in sulphur chloride, saturated at the ordinary temperature, is heated at about $150°$ and then cooled, it is found that a further and considerable quantity of sulphur may be dissolved in the liquid.   It is shown that this cannot be due to the formation of S_μ from S_λ, for the solubility of S_μ in sulphur chloride is very small at the ordinary temperature, and if solutions saturated with S_μ at a higher temperature are cooled down, this separates out quite readily.

In order to ascertain whether this phenomenon is due to the formation of a new modification of sulphur or to the combination of sulphur with the sulphur chloride, systematic determinations have been made of the solubility of rhombic sulphur in sulphur chloride which has been heated with varying proportions of sulphur at a definite temperature and then cooled to either $25°$, $0°$, or $-60°$. The data thus obtained point to the formation of a new variety of sulphur. If this conclusion is correct, it should be possible to obtain some indication of its formation in the absence of sulphur chloride.   This is actually the case, for if sulphur is heated alone to $125°$ and rapidly cooled, and its solubility in sulphur chloride examined, it is found that the solubility is distinctly greater than that of unheated rhombic sulphur.
                                                        H. M. D.

The Relation between the Sulphur Modifications. H. L. DE LEEUW (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 584—593). —If the sulphur contained in a dilatometer tube is heated to its boiling point, and then rapidly cooled so that a large proportion of the

S_μ formed remains intact, it is found that the temperature of conversion of rhombic into monoclinic sulphur is lowered from 95·45° to about 71°. As the proportion of S_μ present decreases, the transition temperature rises until it reaches 95·45°, which must be regarded as the true unary transition point. Kruyt's work (A., 1911, ii, 879 ; 1912, ii, 1051) on the dynamic allotropy of sulphur is criticised adversely, and in particular it is shown that there is no evidence for the assumption of a region of partial miscibility in the liquid phase.

The occurrence of two liquid layers is due to differences in temperature, and when the thermal conductivity is increased by the introduction of platinum wire or gauze, the phenomenon in question is only observed very indistinctly or not at all.   H. M. D.

Alleged Complexity of Tellurium. WILLIAM C. MORGAN (*J. Amer. Chem. Soc.*, 1912, **34**, 1669—1675).—Flint (A., 1910, ii, 845 ; 1912, ii, 1051) has stated that by fractional hydrolysis of tellurium tetrachloride, he obtained two fractions, one giving the atomic weight 124·3, and the other, which was still impure, the atomic weight 128·85. This work has now been repeated with a large quantity of material, but the results do not show progressive diminution of the atomic weight, and thus fail to confirm Flint's conclusion. In view of these experiments and those of other investigators, the author considers that the evidence for the homogeneity of tellurium is quite convincing.   E. G.

[Compounds of Tellurium and Iodine.] FRANS M. JAEGER and J. B. MENKE (*Zeitsch. anorg. Chem.*, 1912, **77**, 320. Compare A., 1912, ii, 344).—It is not possible to determine the freezing point of mixtures containing more than 70% of tellurium in an open vessel, and mixtures rich in iodine boil. The compound TeI_4 dissociates when heated in carbon dioxide.   C. H. D.

The Ternary System Tellurium Tetra-iodide–Hydrogen Iodide–Iodine, and the Estimation of Tellurium by means of Hydrazine Hydrate. J. B. MENKE (*Zeitsch. anorg. Chem.*, 1912, **77**, 282—288. Compare Jaeger and Menke, A., 1912, ii, 344).— Tellurium tetra-iodide, prepared by melting together its components, is heated with hydriodic acid and iodine in a sealed glass tube, ten days being allowed for the attainment of equilibrium in each experiment. The only solid phases found are $TeI_4,HI,8H_2O$ and iodine. A hexa-iodide is thus not obtained either by fusion or from solution. The double compound resembles iodine in appearance.

For analysis, the free iodine is titrated with thiosulphate after neutralisation with sodium hydrogen carbonate ; the total iodine is estimated as silver iodide after removal of most of the tellurium by alkali sulphite. The method of Gutbier and Flury (A., 1902, ii, 653) is not applicable to tellurium tetra-iodide, and the reduction of tellurium by means of sulphur dioxide is not exact, as the fine, amorphous tellurium readily oxidises. Precipitation by means of hydrazine hydrate is usually incomplete, as the filtrate contains colloidal tellurium. In acid solution the precipitation is almost complete, but the excess of acid must be neutralised before filtration, otherwise the precipitate partly redissolves.   C. H. D.

The Validity of Werner's Theory of Subsidiary Valencies for Ammoniates. WALTER PETERS (*Zeitsch. anorg. Chem.*, 1912, 77, 137—190).—The addition of ammonia to inorganic salts has been studied by means of the apparatus of Ley and Wiegner (A., 1905, i, 749). After saturating the solid with ammonia, it is weighed, transferred to a vacuum until the weight is constant, and again saturated. Addition takes place more readily the second time, and in some cases a further quantity of ammonia is added.
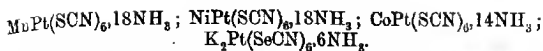
The number of molecules added depends on the degree of saturation of the salt molecule and on the residual affinity of its ions, and when salts with the same anion but different cations are compared, analogies corresponding with the periodic system are observed. The number of molecules of ammonia is most frequently six or a multiple of six, which is in accordance with Werner's hypothesis.

The following new compounds have been prepared :

$CuCl,3NH_3$; $CuBr,3NH_3$; $CuI,3NH_3$; $CuCN,\frac{1}{2}NH_3$;
$$Cu(NO_3)_2,5NH_3 ;$$

$AgCl,3NH_3$; $AgBr,2\frac{1}{2}NH_3$; $AgI,\frac{1}{2}NH_3$; $AgCNO,NH_3$; $AgCNS,2NH_3$;
$AgNO_3,3NH_3$; $KAuCl_4,3NH_3$; $KAu(CNS)_2,5NH_3$; $ZnSO_4,H_2O,6NH_3$;
$K_2HgI_4,2NH_3$; $BaHgI_4,8NH_3$; $Cu_2HgI_4,6NH_3$; $CdHgI_4,6NH_3$;
$Hg(CNS)_2,4NH_3$; $Hg(C_2H_3O_2)_2,4NH_3$; $Hg(C_3H_5O_2)_2,4NH_3$;
$$CrCl_2,6NH_3 ;$$

$UCl_4,3NH_3$; $UO_2Cl_2,2NH_3$; $MnCl_2,6NH_3$; $MnI_2,6NH_3$;
$$MnSO_4,6NH_3 ;$$

$MnSO_4,H_2O,5NH_3$; $FeSO_4,H_2O,5NH_3$; $Zn_2Fe(CN)_6,7NH_3$;
$$Mn_2Fe(CN)_6,2NH_3 ;$$

$Cd_2Fe(CN)_6,7NH_3$; $Co_2Fe(CN)_6,3NH_3$; $Ni_2Fe(CN)_6,7NH_3$;
$$Zn_3[Fe(CN)_6]_2,12NH_3 ;$$

$Mn_3[Fe(CN)_6]_2,6NH_3$; $Cu_3[Fe(CN)_6]_2,16NH_3$; $Cd_3[Fe(CN)_6]_2,12H_2O$;
$Co_3[Fe(CN)_6]_2,8NH_3$; $Na_2FeNO(CN)_5,2NH_3$; $Ni(SCN)_2,6NH_3$;
$$NiS_2O_6,6NH_3 ;$$

$Co(CN)_2,2NH_3$; $Co(SCN)_2,6NH_3$; $RuCl_3,3NH_3$; $RuBr_3,3NH_3$;
$$RhCl_3,4NH_3 ;$$

$PdCl_2,5NH_3$; $PdI_2,6NH_3$; $Na_2PdCl_4,5NH_3$; $(NH_4)_2PdCl_4,5NH_3$;
$PtCl_2,5NH_3$; $PtI_2,6NH_3$; $Na_2PtCl_4,4NH_3$; $Ag_2PtCl_4,6NH_3(7\frac{1}{2}NH_3$ at low temperatures$)$; $K_2Pt(CN)_4,NH_3$; $KNaPt(CN)_4,2NH_3$;
$$CuPt(CN)_4,4NH_3 ;$$

$Ag_2Pt(CN)_4,5NH_3$; $MgPt(CN)_4,4NH_3$; $BaPt(CN)_4,6NH_3$;
$ZnPt(CN)_4,4NH_3$; $CdPt(CN)_4,6NH_3$; $MnPt(CN)_4,4NH_3$;
$$FePt(CN)_4,4NH_3 ;$$

$NiPt(CN)_4,6NH_3$; $CoPt(CN)_4,6NH_3$; $CaPt(CN)_4,3NH_3$;
$$K_2Pt(SCN)_6,2NH_3 ;$$

$CuPt(SCN)_4,8NH_3$; $Ag_2Pt(SCN)_4,6NH_3$; $PtCl_4,6NH_3$; $PtBr_4,6NH_3$;
$Na_2PtCl_6,6NH_3$; $Ag_2PtCl_6,8NH_3(10NH_3$ at $-10°)$; $CuPtCl_6,18NH_3$;
$CaPtCl_6,12NH_3$; $BaPtCl_6,6NH_3$; $ZnPtCl_6,11NH_3$; $CdPtCl_6,18NH_3$;
$MnPtCl_6,11NH_3$; $NiPtCl_6,12NH_3$; $CoPtCl_6,12NH_3(18NH_3$ at $-20°)$;
$Na_2PtBr_6,6NH_3$; $K_2Pt(SCN)_6,12NH_3$; $(NH_4)_2Pt(SCN)_6,15NH_3$;
$CuPt(SCN)_6,15NH_3$; $Ag_2Pt(SCN)_6,14NH_3$; $Au_2[Pt(SCN)_6]_3,30NH_3$;
$BaPt(SCN)_6,12NH_3$; $ZnPt(SCN)_6,15NH_3$; $CdPt(SCN)_6,18NH_3$;
$$Tl_2Pt(SCN)_6,9NH_3 ;$$

$MᵤPt(SCN)_6,18NH_3$; $NiPt(SCN)_6,18NH_3$; $CoPt(SCN)_6,14NH_3$;
$K_2Pt(SeCN)_6,6NH_8$.

Hydrogen chloride and hydrogen phosphide are not absorbed by any inorganic salts under similar conditions.

The absorption spectra of aqueous solutions of the compounds $CuCl_3,6NH_3$ and $CuPtCl_6,18NH_3$ show that both the long visible waves and the ultra-violet are absorbed, the transmitted band being narrower in the case of the double salt.

Determinations of the vapour pressure of several of the compounds have been made by means of a tensimeter.   C. H. D.

Revision of the Atomic Weight of Phosphorus. III. Analysis of Phosphorus Trichloride. GREGORY P. BAXTER and CHARLES J. MOORE (*J. Amer. Chem. Soc.*, 1912, 34, 1644—1657).—In earlier papers (Baxter and Jones, A., 1910, ii, 288; Baxter, Moore, and Boylston, A., 1912, ii, 347), accounts have been given of determinations of the atomic weight of phosphorus by the analysis of silver phosphate and phosphorus tribromide. The investigation has now been extended to the analysis of phosphorus trichloride.

Phosphorus trichloride was prepared and analysed by methods similar to those employed in the case of the tribromide. The product was freed from the pentachloride by distillation in a vacuum. Two series of fractions were collected, and analysed in the usual way after decomposition with water and oxidation of the phosphorous acid produced.

From the average of twenty-four analyses, the value for the atomic weight of phosphorus was found to be $31·018$ ($Ag = 107·880$; $Cl = 35·457$), as compared with $31·04$ obtained from the analysis of silver phosphate and $31·027$ from that of phosphorus tribromide. The average of the results from the tribromide and trichloride is $31·023$.
                                                                E. G.

The Density of Phosphorus Vapour. ALFRED STOCK, GEORGE E. GIBSON, and ERICH STAMM (*Ber.*, 1912, 45, 3527—3539).—A membrane-manometer, which is a special modification of the spiral manometer of Ladenburg and Lehmann (*Ber. Deut. physikal. Ges.*, 1906, 4, 20), and is to be described in another paper, was used to determine the vapour density of phosphorus; the manometer is sensitive to $0·5$ mm. difference in pressure. Purified red phosphorus, which can be obtained in a purer condition than colourless phosphorus, was used in the experiments, at the temperature of which it was completely transformed into vapour.

At temperatures between $500°$ and $700°$ the vapour density corresponds exactly with the formula P_4. At higher temperatures dissociation takes place, but even at $1200°$ it is only 61% under a pressure of 175 mm. Calculations made on the assumption that the dissociation which occurs is in accordance with the equation: $P_4 \rightleftharpoons 2P_2$, give a very good agreement between theory and experiment. Under atmospheric pressure the degrees of dissociation at $800°$, $1000°$, and $1200°$ are respectively $0·01$, $0·1$, and $0·33$; under a

pressure of 0.25 atmos. the degree of dissociation is almost 0.66 at $1200°$.

Calculation of the heat of dissociation gives values varying from $-49,200$ to $-50,300$ cals.

The above results do not agree with previous measurements, but various measurements were so concordant that there is every probability of their accuracy. The experiments of Preuner and Brockmöller (A., 1912, ii, 1146) are prohably untrustworthy because they used ordinary, commercial phosphorus.   T. S. P.

Boron Hydrides. ALFRED STOCK and CARL MASSENEZ (*Ber.*, 1912, 45, 3539—3568).—The boron hydrides obtained by the authors have been prepared by the action of hydrochloric acid on magnesium boride.

Full details are given of the conditions needful for the preparation of a satisfactory sample of magnesium boride from magnesium and boron trioxide.

The decomposition of the boride with acid was carried out in an apparatus similar to that used in the preparation of antimony hydride (A., 1904, ii, 246), the boride being dropped continuously into the acid whilst a slow stream of hydrogen is passed through the apparatus. The decomposition is carried out at $50°$, using $4N$-hydrochloric acid. The evolved gases are passed through U-tubes immersed in liquid air, a snow-like deposit forming, whilst hydrogen passes on. The first portions of gas escaping from the U-tube smell strongly of boron hydride, but as soon as the solid forms it prevents the escape of any more hydride. The deposit consists of boron hydrides, together with silicon hydrides and carbon dioxide from impurities in the materials used. It is fractionally distilled at varying pressures and temperatures in order to remove the impurities. Hydrogen and traces of silicon hydride are removed by evacuating at the temperature of liquid air. The temperature is then raised to $-80°$, when the solid melts to a colourless, strong refracting liquid, having a pressure of 250 mm. The pressure can be rapidly dimioished to a few millimetres, whereby silicon hydrides, carbon dioxide, and any traces of hydrogen phosphide or sulphide which may be present are removed. As soon as the gas is free from silicon hydride, it is collected separately at a pressure of less than 3 mm., the temperature of the room in which the distillation is being carried out being maintained above $20°$, otherwise liquid hydride would be condensed in the mercury pump used. The gas collected at this pressure and temperature consists of the *boron hydride*, B_4H_{10}. The residue is then warmed to $-40°$ and distilled until the pressure falls to $1\frac{1}{2}$ mm., the temperature further raised to $0°$, and distillation proceeded with until the pressure falls to 9—10 mm., in order to remove all the hydride B_4H_{10}. The remaining liquid on further distillation gives the *boron hydride*, B_6H_{12}, the pressure falling below 5 mm. Two hundred grams of magnesium boride give about 100 c.c. of the pure hydride B_4H_{10}, and 60 mg. of the hydride B_6H_{12}.

Owing to the fact that these hydrides possess compositions very

different from what was to be expected, thoy were analysed by a number of different methods.

The hydride B_4H_{10} was analysed as follows: (1) a known volume was decomposed by passing slowly through a weighed quartz tube at $500°$ and the hydrogen collected. The boron was weighed directly, and also oxidised to boric acid and estimated volumetrically; (2) at room temperature the gas is slowly decomposed by water, with liberation of hydrogen and formation of boric acid. The results are in accordance with the equation: $B_4H_{10} + 12H_2O = 4B(OH)_3 + 11H_2$. (3) Decomposition also takes place in the presence of sodium hydroxide, the results according with the equation: $B_4H_{10} + 4NaOH + 4H_2O = 4NaBO_2 + 11H_2$. The vapour density agrees with the formula B_4H_{10}.

The boron hydride B_4H_{10} is a colourless liquid, b. p. $16—17°/760$ mm., m. p. $ca -112°$, of a peculiar and most disagreeable odour. A few bubbles of the gas affect respiration and cause headache. It is a very unstable substance, decomposing at the ordinary temperature after a few hours, and quicker at higher temperatures, giving rise to a whole series of new hydrides which await investigation. It is similarly decomposed by electric sparks. It takes fire spontaneously in the air or in oxygen, burning with a green flame. Water and dilute hydrochloric acid decompose it, and it is oxidised by concentrated nitric acid with explosive violence. It is rapidly absorbed by aqueous sodium hydroxide, the solution slowly evolving hydrogen in accordance with the equation already given. It is probable that an intermediate hypoborate, corresponding with the oxide B_4O_5 (compare Travers and Ray, A., 1912, ii, 938), is formed, since when brought into contact with solid potassium hydroxide the latter becomes coated with a thick layer of a white salt in the form of a loose powder.

Ammonia gives a solid light brown substance, insoluble in water, whilst alcohol decomposes the hydride with evolution of hydrogen. The solution in benzene is very stable towards oxygen.

The hydride B_6H_{12} was analysed similarly to the hydride B_4H_{10} by decomposing it by heat. The vapour density corresponds with the formula B_6H_{12}. It is a colourless liquid, b. p. $10°/15$ mm., ca $100°/760$ mm., possessing a highly disagreeable odour and taking fire spontaneously in the air. It is more sensitive towards water and moisture than the hydride B_4H_{10}. With aqueous alkalis, hydrogen is immediately evolved.

The composition of the above hydrides is not in agreement with that of the boron alkyls, nor with the results obtained by Jones and Taylor (T., 1881, 39, 213), Sabatier (A., 1891, 979), and Ramsay and Hatfield (P., 1901, 17, 152). A critical examination of the experiments of these various investigators shows that no trustworthy conclusion can be drawn from them as to the composition of boron hydride.   T. S. P.

Condition Diagram of Carbon Dioxide. GUSTAV TAMMANN (*Chem. Zentr.*, 1912, ii, 598; from *Nachr. K. Ges. Wiss. Gött.*, 1912, 446—452).—The author had observed previously that liquid carbon

dioxide at temperatures ranging from $-56.7°$ to $-7.5°$ and pressures
between 5·1 atm. and 2800 kg. per sq. cm. deposited a different
crystalline species from that obtained at higher pressures.   Repetition
of the experiments up to 4000 kg. pressure showed that a triple point
does not occur in the melting curve (compare A., 1912, ii, 29).

<div align="right">T. A. H.</div>

Carbon Subsulphide, C_3S_2.   ALFRED STOCK and PAUL PRAETORIUS
(*Ber.*, 1912, **45**, 3568—3578).—In the preparation of carbon telluride
(A., 1911, ii, 722) a substance possessing a very penetrating odour was
always an accompanying product.   This has proved itself to be the
tricarbon disulphide, C_3S_2, first obtained by Lengyel (A., 1894, ii, 90),
which the authors propose to call carbon subsulphide from analogy
to carbon suboxide.

Lengyel's method of preparation (*loc. cit.*) is not a convenient one,
and the authors have sought for a better.   The compound is produced
when an arc is formed between carbon electrodes under liquid carbon
disulphide, but it is accompanied by many by-products.   It is also
produced when carbon disulphide is passed through a heated quartz
tube, the most favourable temperature being $1000—1100°$; carbon is
deposited in the tube at the same time, and diminishes the yield of
subsulphide.   If the quartz tube is filled with a spiral of iron wire,
the formation of subsulphide takes place below 800°, but it soon
ceases owing to the formation of iron sulphide.   The action of metals
led the authors to investigate the formation of subsulphide by the
disintegration of metals by means of an arc under liquid carbon
disulphide, the disintegration of the anode exposing fresh, hot surfaces
continually to the carbon disulphide.   Iron, copper, and aluminium
electrodes gave no subsulphide, whilst electrodes of arsenic, bismuth,
lead, tin, antimony, cadmium or zinc yielded the required compound,
large quantities of the metallic sulphides being formed at the same
time.   The best results were obtained with a carbon cathode and an
anode consisting of antimony mixed with 7% of carbon.   The brownish-
red solution obtained is filtered, and then shaken with mercury and
phosphoric oxide to remove sulphur and polysulphides and water.   A
solution of carbon subsulphide in carbon disulphide is thus obtained,
from which by distillation, finally under a high vacuum, the pure
substance is obtained in a receiver cooled to $-40°$ as a yellowish-red
solid.   At the ordinary temperature, it forms a bright red, strongly
refracting liquid, the vapour density of which corresponds with the
formula C_3S_2; the m. p. is $-0.5°$, and the substance possesses
normal molecular weight in carbon disulphide solution.

The alcoholic solution decomposes after a short time.   Dilute
solutions in carbon disulphide are salmon-coloured, stronger solutions,
yellowish-brown ; above 1% strength the solutions gradually deposit
black, polymerisation products, even in the dark ; solutions below 1%
strength are stable in the dark, but not in sunlight.   Carbon disul-
phide solutions have no action on copper or mercury, but are decom-
posed by the sulphides of these metals, owing, probably, to the
formation of additive products.

The polymerisation at $90°$ is a reaction of the second order, and

can be readily measured by observing the diminution in pressure ; the reaction takes place at the surface of the containing vessel.

Carbon suhsulphide can he considered as the anhydride of thiomalonic acid (compare carbon suhoxide), since with aniline it readily gives thiomalonanilide. Its constitution may therefore be expressed as $S{:}C{:}C{:}C{:}S$.

The hlack polymerisation product is not affected by water, sodium hydroxide, hydrochloric acid, or chlorine water. Heated in a vacuum it gives carbon disulphide and a hlack residue which still contains 39% of sulphur. T. S. P.

The Reduction of Silica. H. VON WARTENBERG (*Zeitsch. anorg. Chem.*, 1912, '79, 71—87).—Platinum is often attacked when heated in a silica vessel in a reducing atmosphere, oven if not in contact with the silica, indicating the formation of either silicon vapour or silicon hydride. The dissociation of silicon hydride (prepared by the action of alcohol on purified silicon-chloroform, followed by decomposition of the ester by sodium) has heen studied. It is necessary to use a catalyst, and the nickel used in Sahatier's method of reduction has proved to be suitable. Without a catalyst, decomposition is hardly measurable helow 350°, even after several days. Monsurements up to 380° give the result $SiH_4 = Si + 2H_2 - 8700$ cal. From 100° to 150° the pressures observed are higher than would be expected, probably owing to the occurrence at the lower temperature of the reaction $2SiH_4 = Si_2H_4 + 2H_2$.

The volatilisation of crystallised silicon in a stream of hydrogen has been measured up to 1315°. Silicon hydride is not to be detected in the issuing gas. The experiment has heen repeated with argon in place of hydrogen, with similar results, the diminished loss of silicon being accounted for by the formation of a thin protecting layer of the nitride, Si_3N_4, as nitrogen is not completely removed from argon, even by passing over heated lithium. The value $SiH_4 = Si$ (vapour) $+ 2H_2 - 44,000$ cal. is calculated.

The reduction of silica by hydrogen has been studied at 1350—1400°, at which temperature silica is not volatile. The observed suhlimation at lower temperatures is therefore due to reduction followed by oxidation. Carhon monoxide and graphite are also capable of reducing silica. C. H. D.

The Velocity of Crystallisation and Crystallising Power of Silicates. ERWIN KITTL (*Zeitsch. anorg. Chem.*, 1912, 77, 335—364). —The crystallisation of a numher of silicates has been examined in relation to the viscosity. Crystallisation takes place on the heating stage of a microscope, and the growth of the crystals, which usually form radiating groups of needles, is measured by means of a micrometer eyepiece. The linear velocity of crystallisation varies with the undercooling in the manner described by Tammann for organic substances. The horizontal maximum of the curve is often very short, or diminished to a point, and is best marked in silicates of low viscosity. Olivine, hronzite, and hypersthene show sharp maxima, whilst polysilicates show a low, flat curve. The maximum is usually 20—30° below the initial temperature of crystallisation. Metasilicates

form the longest needles, the larger number of centres in orthosilicates causing interference.

Orthosilicates of the alkalis form glasses without crystallising, with the exception of lithium orthosilicate, which crystallises if cooled slowly. Simple and mixed magnesium, calcium, ferrous, and manganous silicates crystallise readily. Alkali metasilicates, with the exception of lithium, form only glasses. The simple metasilicates of the metals mentioned above crystallise readily, whilst the mixed metasilicates remain partly glassy. Polysilicates, especially those of complex constitution, tend to form glasses.   C. H. D.

The Proportion of Potassium Chloride in Potassium Chlorate, and the Nephelometric Control. FRIEDRICH MEYER and ARTHUR STÄHLER (*Zeitsch. anorg. Chem.*, 1912, **77**, 255—256. Compare A., 1911, ii, 881; Guye, A., 1912, ii, 552).—The criticism of Guye overlooks the fact that the solution in the nephelometer is not one of silver chloride in pure water, but contains an excess of either silver or chloride, considerably diminishing the solubility. In the case of potassium chlorate, the error cannot affect more than the sixth decimal place in the atomic weight of chlorine or potassium.

C. H. D.

Molten Carnallite. KURT ARNDT and HEINRICH HUGO KUNZE (*Zeitsch. Elektrochem.*, 1912, **18**, 994—998).—Determinations of the density, electrical conductivity, and freezing point of carnallite and mixtures of carnallite and potassium chloride are given. The carnallite used was prepared artificially by mixing magnesium chloride and potassium chloride in the requisite proportions. In all experiments decomposition of the magnesium chloride was prevented by the constant and careful addition of small quantities of ammonium chloride. The freezing points were deduced from cooling curves obtained by the use of a thermocouple, and are as follows: pure carnallite, 496°; carnallite + 6% KCl, 493°; carnallite + 12% KCl, 484°; carnallite + 18% KCl, 470°; carnallite + 24% KCl, 460°, and carnallite + 30% KCl, 436°. The density determinations were made by weighing a platinum sinker in the molten mixture (compare Brunner, A., 1904, ii, 244). Tables of results are given which show that at 550°, 650°, and 750° the addition of potassium chloride up to 30% causes a slight decrease in the density of the mixture. Pure carnallite has the density at 570°, 1·711; 600°, 1·698; 650°, 1·678; 700°, 1·658; 750°, 1·638, and 780°, 1·625. It is shown from the density determinations that carnallite and potassium chloride form no definite compounds. The conductivity measurements were made by the method described by Arndt (A., 1906, ii, 418), and the following specific conductivities obtained:

%-Excess of potassium chloride.

Temp.	20·3—20·5.	10·4—10·7.	0·8—1·0.
550°	0·96	0·92	0·87
600	1·07	1·03	0·98
650	1·18	1·14	1·09
700	1·29	1·25	1·20
750	1·40	1·36	1·31

By extrapolation from the above figures the specific conductivity of pure carnallite was deduced. The values are at 570°, 0·92; 600°, 0·97; 650°, 1·08; 700°, 1·20, and 780°, 1·37.   J. F. S.

Thermal Analysis of Binary Mixtures of Alkali Nitrites with Other Salts of the Same Metals. D. MENEGHINI (*Gazzetta*, 1912, **42**, ii, 472—479).—The paper deals with the thermal analysis of the systems KNO_2–KNO_3, $NaNO_2$–$NaCl$, and $NaNO_2$–$NaBr$. Fused mixtures of potassium nitrite and nitrate, in the interval from 10% to 100% of nitrate, give an uninterrupted series of mixed crystals, whilst at the ordinary temperature between the same limits of concentration there is no miscibility. It is impossible to obtain nitrite free from nitrate.

The experiments with sodium nitrite were carried out with a nitrite containing 1·5% of nitrate. The diagrams of the systems $NaNO_2$–$NaCl$ and $NaNO_2$–$NaBr$ belong to Roozeboom's type III.
                                                R. V. S.

The Action of Ozone on Alkali Hydroxides. WILHELM TRAUBE (*Ber.*, 1912, **45**, 3319—3320. Compare A., 1912, ii, 844).— The previous work of Manchot and Kampschulte (A., 1908, ii, 101) on the same subject is acknowledged.   T. S. P.

The Electrolytic Preparation of Sodium Hypochlorite. PAUL H. PRAUSNITZ (*Zeitsch. Elektrochem.*, 1912, **18**, 1025—1080).— After careful consideration of the theory of the electrolytic production of sodium hypochlorite from sodium chloride the paper deals first with an experimental examination under laboratory conditions, with enclosed cells, of the various factors which influence the reaction. In the second part the results are applied to the technical conditions, the author using in this connexion working models of the best known technical electrolysers. The experiments were all made, except where the contrary is stated, with 5N-solutions of sodium chloride to which a 0·2N-solution of potassium chromate had been added. The reactions were studied with regard to the maximum concentration of available bleaching chlorine obtainable and the current efficiency. The first section includes: (g) The influence of the anode current density (D_a) and the anode shape. The best results were obtained with a short bright platinum anode in the form of a wire, in which case a maximum concentration of 88 grams per litre of available bleaching chlorine was obtained with a current density $D_a = 14·3$ amperes per sq. cm. Massive platinum anodes (sheets or wires) are far more efficient than gauze electrodes. Platinised platinum anodes showed a slight superiority over bright anodes for current densities up to $D_a = 0·44$ ampere per sq. cm., but above this value there was no advantage gained by platinising the electrodes. With $D_a = 0·44$ ampere per sq. cm. using platinised electrodes a maximum concentration of 48 grams per litre available bleaching chlorine was obtained with a current efficiency of 91%. The platinised electrodes showed their superiority, especially when they had been previously cathodically polarised. Grey platinum electrodes behaved similarly to the platinum-black electrodes.

(*b*) Influence of temperature. The best results were obtained at the ordinary temperature. At 30° the concentration of hypochlorite was diminished, whilst at 0° and 15° the formation of chlorine hydrate $(Cl_2, 10H_2O)$ on the anode interfered with the process. (*c*) Influence of stirring the electrolyte. The effect of stirring is to reduce the maximum concentration of the hypochlorite. (*d*) Influence of dilution of the electrolyte. The salt concentration was changed from $5N$ to $2N$ and $1·1N$; in each case there was a decrease in the maximum concentration of the hypochlorite and of the current efficiency. (*e*) Influence of the addition of various substances to the electrolyte. The object of the addition was to prevent cathodic reduction. The experiments were carried out with carbon anodes in addition to platinum which had hitherto been used. The results are: (1) Potassium chromate prevented reduction almost entirely ; (II) the addition of calcium chloride and Turkey-red oil (sulphonated castor nil) allowed a reduction of 20%, although a 30% higher maximum concentration of hypochlorite could be obtained. The action of the Turkey-red oil is probably the formation of an anode coating which causes a great increase of the current density. The best results are obtained by combining the chromate and Turkey-red oil additions ; in this way, for example, 62 grams per litre of available bleaching chlorine was obtained with a 62% current efficiency. By using Portland cement to make the cell walls of, from which something is dissolved, an improvement of both anode and cathode actions was effected. Wheat starch and soluble starch gave much inferior results. The author experimented with models of the apparatus used in the old Kellner process, the new Kellner process, the Schuckert process, and the Weichert process. Working with the old Kellner process it was found that the highest concentration of hypochlorite obtainable was 12—20% below that given in closed vessels. This is attributed to the influence of the carbon dioxide from the air and to the circulation of the electrolyte over the anode. In the new Kellner process it was found that the maximum hypochlorite concentration was independent of the current density and the rate of flow of the electrolyte. The anode in this process must be placed beneath the cathode for the best results. The yield is increased by the addition of potassium chromate and Turkey-red oil to the electrolyte, and in this case a concentration of 68 grams per litre available bleaching chlorine was obtained from a $5N$-solution of sodium chloride with a 41% current efficiency. In the Schuckert process the current density has but little influence on the concentration of the product ; the best results were achieved by adding potassium chromate to the electrolyte. The addition of calcium chloride and sodium resinate gave less favourable results. In the Weichert process, using a dilute sodium chloride solution (5·5° Bo) with the addition of 0·2% potassium chromate, a yield of 8—10 grams per litre of available bleaching chlorine was obtained when working with a current of 14 amperes at 95 volts, and with the electrolyte flowing through the cell at 40 litres per hour.

J. F. S.

Crystallographic Study of Lithium Chlorate. (Mlle.) H. BRUNL (*Bull. Soc. franç. Min.*, 1912, **35**, 155—165).—Lithium chlorate

was prepared by mixing solutions of lithium sulphate and barium chlorate. It is extremely deliquescent and is very soluble in alcohol, the latter property affording a means of purifying the salt. Under the microscope the anhydrous salt, $LiClO_3$ (m. p. 125—127·5°), was observed in three different crystalline modifications. There is also the hydrate, $Li_2ClO_3,\tfrac{1}{2}H_2O$ (m. p. 63—65°), which forms plates with secondary twin-lamellæ. L. J. S.

The Binary System Li_2SiO_3–$Al_2(SiO_3)_3$. REZSÖ BALLÓ and EMIL DITTLER (*Zeitsch. anorg. Chem.*, 1912, 77, 456. Compare A., 1912, ii, 758).—The biaxial modification of lithium metasilicate previously described is already known, and is probably monoclinic. Its properties persist in its solid solution with aluminium metasilicate. C. H. D.

The Carbonic Acid of Natural Waters which is Able to Attack Calcium Carbonate. J. TILLMANS and O. HEUBLEIN (*Chem. Zentr.*, 1912, ii, 1395—1396; from *Gesundheits-Ing.*, 1912, 35, 669—677).—A certain amount of carbonic acid is necessary to protect calcium hydrogen carbonate from decomposition, so that, although "free," it does not attack calcium carbonate. Thus a soft water will attack limestone far more than a hard water containing the same amount of free carbon dioxide. A curve has been made, connecting calcium hydrogen carbonate with the carbon dioxide which is necessary for its protection. Having found the amount of combined carbon dioxide and the total free carbon dioxide in a water, it is thus possible to say how much of the latter is capable of attacking calcium carbonate. Small amounts of magnesium carbonate do not seriously affect the results. J. C. W.

Physical Action of Neutral Reagents on the Tribasic Alkaline Earth Phosphates. Investigation of the Colloidal State. WILLIAM OECHSNER DE CONINCK (*Rev. Gen. Chim. Pure Appl.*, 1912, 15, 285—286).—If the normal phosphates of calcium, strontium, and barium are shaken up with water, methyl alcohol, or ethyl alcohol for several days, colloidal solutions are obtained which can be separated from the excess of phosphate by filtration through filter paper. In this way the author has prepared colloidal solutions of calcium phosphate in water and methyl alcohol and of strontium phosphate in methyl and ethyl alcohol. The solutions are unstable, and on this account the solutions of barium phosphate, which appear to be formed in methyl and ethyl alcohols, are coagulated during the process of filtration. H. M. D.

The Ternary Alloys of Magnesium, Zinc, and Cadmium. GIUSEPPE BRUNI and CARLO SANDONNINI (*Zeitsch. anorg. Chem.*, 1912, 78, 273—297).—The portion of this system which includes the constituents Zn–Cd–$MgZn_2$ has been described previously (A., 1910, ii, 954). Cadmium retains up to 2 atomic % of zinc in solid solution. The crystallisation-interval is very small throughout the magnesium–cadmium series. A transformation curve for the compound $MgCd$ is

drawn, showing a eutectoid point near 80 atom. % Cd, traces of a eutectoid structure being recognisable in slowly-cooled alloys having about this composition.

ᐧ The compounds $MgZn_2$ and MgCd form a simple eutectiferous series. The entire triangular diagram is divided into two parts by a continuous eutectic curve, connecting the two eutectic points of the magnesium-zinc system, and separating the $MgZn_2$ area from that of solid solutions and from that of zinc. This curve passes through a maximum. The curves of secondary and eutectic crystallisation have been completely traced. It appears that the β-solid solutions retain zinc in solution at high temperatures, but that its solubility disappears at about 250°.

The alloys are best etched by means of nitric acid in amyl alcohol. The photo-micrographs illustrate the whole series of ternary alloys, and serve to fix the limits of stability of the solid solutions.

C. H D

Action of Potassium Amide on Thallium Nitrate in Liquid Ammonia Solutions. EDWARD CURTIS FRANKLIN (*J. Physical Chem.*, 1912, 16, 682—703).—The author describes in detail the preparation and properties of thallium nitride and potassium ammonio-thallite which have already been briefly mentioned (A., 1912, ii, 452).

The interaction in liquid ammonia solution of thallium nitrate and potassamide according to the equation: $3TlNO_3 + 3KNH_2 = Tl_3N + 3KNO_3 + 2NH_3$ yields a a dense black precipitate of thallium nitride which is readily soluble in excess of potassamide and also in liquid ammonia solutions of ammonium nitrate. In the latter case the thallium nitride is reconverted into nitrate, thus: $Tl_3N + 3NH_4NO_3 = 3TlNO_3 + 4NH_3.$

From the solution in excess of potassamide well formed, golden-yellow crystals are deposited. These consist apparently of iso-morphous mixtures of potassamide and dipotassium ammoniothallite with ammonia of crystallisation. The potassamide may be eliminated by contact with excess of thallium nitride or by repeated crystallisation.

Dipotassium ammoniothallite, when freed from excess of ammonia in a vacuum at $-40°$, has the formula $TlNK_2,4NH_3$ or
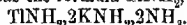
$$TlNH_2,2KNH_2,2NH_3.$$

At $+20°$, in a vacuum, ammonia is given off and the yellow substance, $TlNK_2,2NH_3$ or $TlNH_2,2KNH_2$, results. On further deammoniation at $+100°$ the substance turns black and approximates to the composition $TlNK_2,1\frac{1}{3}NH_3$, alternatively written $Tl_3N,6KNH_2$ or as a simple mixture ($Tl_3N + 6KNH_2$).

The alternative formula for dipotassium ammoniothallite,

$$TlNH_2,2KNH_2,2NH_3,$$
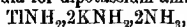
is more reasonable in view of the isomorphous mixed crystals with potassamide, but, on the other hand, thallium amide is unknown in the free state. The extreme composition observed in the mixed crystals was $TlNK_2,4NH_3 : 3.6KNH_2$, and the higher the proportion of potassamide the greater the solubility. The ammonia of crystallisation was always proportional to the thallium content, the proportions being $Tl : 4NH_3$ and $Tl : 2NH_3$ in preparations dried at $-33°$ and $+20°$ respectively.

Thallium nitride and potassium ammoniothallite and its mixtures

explode with great violence when subjected to heat, shock, or the action of water or dilute acids.   They were hydrolysed for analysis by means of water vapour.

No evidence could be obtained of the formation of an amide or imide of thallium even at $-33°$.   R. J. C.

The **Quaternary System** $KCl-CuCl_2-BaCl_2-H_2O$. FRANS A. H. SCHREINEMAKERS and (Miss) W. C. DE BAAT (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 467—472).—The equilibria occurring in this quaternary system have been examined at 40° and 60°.   The choice of these temperatures is determined by the fact that the ternary system $KCl-CuCl_2-H_2O$ is characterised by the formation of only one double salt, $2KCl,CuCl_2,2H_2O$, below 57°, whereas a further double salt, $KCl,CuCl_2$, may occur between 57° and 92°.

The experimental data may be conveniently represented by means of a tetrahedron, the four apices of which correspond with the four components.   The spacial model for 40° shows saturation surfaces corresponding with KCl, $BaCl_2,2H_2O$, $CuCl_2,2H_2O$, and

$$2KCl,CuCl_2,2H_2O,$$

whereas that for 60° shows an additional surface corresponding with $KCl,CuCl_2$.

The temperature corresponding with the disappearance of this surface has been found to be 55·7°, and this temperature corresponds with the reversibility of the change represented by $BaCl_2,2H_2O + /$ $CuCl_2,2H_2O + 2KCl,CuCl_2,2H_2O \rightleftharpoons KCl,CuCl_2 + $ solution.

H. M. D.

Mutual Solubilities of Cuprous Chloride and Ferrous Chloride, as also of Cuprous Chloride and Sodium Chloride, and the Transformation Point of $FeCl_2,4H_2O \rightleftharpoons FeCl_2,2H_2O + 2H_2O$. ROBERT KREMANN and F. NOSS (*Monatsh.*, 1912, **33**, 1205—1215).—At 21·5° the solubility of cuprous chloride is increased by the addition of ferrous chloride, as also that of ferrous chloride by the addition of cuprous chloride, the solid phases in equilibrium with the solution being respectively cuprous chloride and ferrous chloride ; there is no formation of a double salt.   The solution saturated with respect to both the salts contains 73·20 grams of ferrous chloride (anhydrous) and 23·20 grams of cuprous chloride in 100 grams of water.

The system : cuprous chloride–sodium chloride–water at 26·5° behaves similarly to the system : ferrous chloride–cuprous chloride–water.   At the point where it is simultaneously saturated with respect to the individual salts, it contains 57·21 and 44·14 grams of cuprous chloride and sodium chloride respectively per 100 grams of water.

The transformation point of the system $FeCl_2,2H_2O + 2H_2O \rightleftharpoons FeCl_2,4H_2O$, as determined by cooling curves, was found to be 65·2°.

T. S. P.

Ammoniacal Sodium Cuprous Trithionate. KSHITIBHUSHAN BHADURI (*Zeitsch. anorg. Chem.*, 1912, **78**, 327).—Copper sulphate is precipitated with ammonia, and the precipitate is washed and dissolved in ammonia.   Sodium thiosulphate is added, and after remaining over-night, blue crystals are obtained, the solution becoming colourless.

The product, after washing with water and alcohol and drying, forms sky-blue crystals, soluble in water or more readily in ammonia, and giving the reactions of a trithionate. The salt has the composition $3Cu_2S_2O_6,2Na_2S_2O_6,9NH_3$.   C. H. D.

The System $HgCl_2$-$CuCl_2$-H_2O. Frans A. H. Schreinemakers and J. C. Thonus (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 472—474).—In order to ascertain whether mercuric chloride and cupric chloride form a double salt, the form of the solubility isotherm has been determined by a series of solubility measurements at 35°. The composition of the residual "solid phase" as well as that of the solution was determined, and the numbers so obtained show that no double salt is formed at this temperature. A solution containing 21·5% of cupric chloride and 50·5% of mercuric chloride is saturated both with respect to cupric chloride ($CuCl_2,2H_2O$), and to mercuric chloride. The middle portion of the isotherm, where two solid phases coexist, is of very limited dimensions.

The data show that the solubility of mercuric chloride is greatly increased by the addition of cupric chloride. Whereas, in pure water, the solubility amounts to 8·5%, it increases to 52·8% in presence of 18·06% of cupric chloride. When the quantity of cupric chloride present is further increased, a slight diminution occurs in the percentage amount of dissolved mercuric chloride.   H. M. D.

The Acid Dissociation Constant of Aluminium and Zinc Hydroxides. Roland Edgar Slade (*Zeitsch. anorg. Chem.*, 1912, 77, 457—460. Compare P., 1910, 26, 236; Klein, A., 1912, ii, 351; Hantzsch, *ibid.*, 644).—An approximate calculation shows that aluminium hydroxide must have an acid dissociation constant of at least 10^{-10}, and probably higher, and that zinc hydroxide, in its most stable form, must have a corresponding constant of not less than $0·5 \times 10^{-12}$.   C. H. D.

Ultramarine Compounds. L. Wunder (*Zeitsch. anorg. Chem.*, 1912, 77, 209—238).—The replacement of sodium in blue ultramarine by other metals has been studied by Heumann (A., 1877, ii, 572; 1878, 113; 1879, 437, 692; 1880, 217—367), and has now been further developed. The material is heated with the [reacting solution to 120—180° in a closed glass tube, enclosed in sand in a steel cylinder.

Mercurous nitrate yields a greyish-blue mercuro-ultramarine, which loses mercury on heating and leaves a pure blue residue, which becomes yellow on heating and again blue on cooling, this change being capable of being repeated indefinitely. The product is very stable towards acids. Mercuric salts are reduced by ultramarine. Cadmium yields an olive-green product, whilst lead replaces the sodium completely. Lithium, ammonium, and calcium ultramarines have also been prepared.

The decomposition of ultramarine by alum solutions is not due to the acidity of the latter, but to the intermediate formation of an aluminium derivative. Chromium has the same effect. Ferrous ultramarine is dark greyish-blue, and is readily decomposed by acids.

Yellow phosphorus reduces ultramarine to a leuco-compound, which again becomes blue if heated in air. Red ultramarine is decomposed by acids without evolution of hydrogen sulphide, and is not changed by alum solution. Red ultramarine is best prepared by the action of nitric oxide on the blue compound, sulphur being removed in the process. Violet ultramarine is decomposed by alum, and also by acids, sulphur dioxide being evolved. Dry hydrogen reduces it, sulphur being removed as hydrogen sulphide.

Formulæ are proposed for all these compounds. Red ultramarine is regarded as an acid, the sodium salt of which is the violet compound. The blue compound contains the group Al—S—Na, which is absent from the red. C. H. D.

The Heusler Ferromagnetic Alloys of Manganese. EDGAR WEDEKIND (*Zeitsch. angew. Chem.*, 1912, 25, 2524—2526).—A claim for priority against Heusler (*ibid.*, 2253) in respect to manganese borides, and the magnetic properties of binary compounds of manganese. C. H. D.

Ternary Alloys of Iron–Manganese–Copper. NICOLA PARRAVANO (*Gazzetta*, 1912, 42, ii, 513—531).—Of the three binary systems comprised in the ternary system Fe–Mn–Cu, the system Fe–Cu has been studied by Sahmen (A , 1908, ii. 186), and the others by the author (A., 1912, ii, 1175, and this vol., ii, 58). The system Fe–Mn–Cu belongs to type I of the cases of solubility gaps in ternary systems discussed by Parravano and Sirovich (A., 1911, ii, 705), and in a theoretical discussion the author applies the conclusions there set forth to the construction of diagrams from the experimental results in the present instance. In addition to the diagrams, photographs are given of a number of the ternary alloys, which are thus shown to have the structure to be expected from their position in the space diagram. R. V. S.

Revision of the Atomic Weight of Iron. V. Analysis of Ferric Oxide. GREGORY P. BAXTER and CHARLES RUGLAS HOOVER (*J. Amer. Chem. Soc.*, 1912, 34, 1657—1669).—From analyses of ferric oxide by reduction with hydrogen at 900°, Richards and Baxter (A., 1900, ii, 407) obtained the value 55·88 for the atomic weight of iron. Baxter (A., 1904, ii, 177) analysed ferrous bromide and found the value 55·845 ; on repeating this work with purer material, Baxter Thorvaldson, and Cobb (A., 1911, ii, 287) obtained the result 55·838. Baxter and Thorvaldson (A., 1911, ii, 288) further proved that meteoric and terrestrial iron give identical values.

In the present investigation, ferric oxide was prepared by igniting carefully purified ferric nitrate in a current of air. A weighed quantity of the oxide was reduced to the metal by heating it in a current of hydrogen at 1050—1100° for several hours. Two specimens of ferric nitrate were employed, one containing iron of terrestrial origin, and the other, meteoric iron.

The average of twelve analyses yielded 55·847 as the atomic weight of iron ($O = 16·000$). This when combined with the result obtained

from the analysis of ferrous bromide (Baxter, Thorvaldson, and Cobb, *loc. cit.*) gives the value 55·84. The identity of terrestrial and meteoric iron was confirmed.   E. G.

The System Iron–Carbon. III. ANDREAS SMITS (*Zeitsch. Elektrochem.*, 1912, **18**, 1081—1086. Compare A., 1912, ii, 165, 769).— An answer to Ruff (A., 1912, ii, 917; compare also A., 1911, ii, 897). The remainder of the paper is a theoretical consideration of the results of Wittorf (A., 1912, ii, 259), who shows that the system iron-carbon undergoes two inverse separations by raising the temperature, namely, $C \longrightarrow Fe_4C \longrightarrow FeC \longrightarrow Fe_3C \longrightarrow C$. In this connexion the author discusses the relations of the separations of the substances C, FeC, FeC_2, C, which he shows are successively deposited on raising the temperature. PT curves of the system are given in which two quadruple points are indicated, at both of which graphite, FeC, solution and vapour are in equilibrium. On raising the temperature at the lower point, FeC is formed at the expense of the graphite, whilst at the higher point, graphite is produced at the expense of the FeC. The thermal relationships of the various changes are considered.
                                        J. F. S.

The System Iron–Iron Sulphide. RICHARD LOEBE and E. BECKER (*Zeitsch. anorg. Chem.*, 1912, **77**, 301—319. Compare Treitschke and Tammann, A., 1906, ii, 547).—Ordinary ferrous sulphide always contains free iron and also oxide. A product containing 98·72% FeS is obtained by repeatedly melting natural pyrites. The mixtures are made by fusing this product with Swedish iron in porcelain tubes, using a kryptol furnace.

The equilibrium diagram shows a freezing-point curve of simple form, the two branches meeting in a eutectic point at 985° and 85% FeS. The solid components are practically immiscible on the iron side, whilst solid ferrous sulphide retains about 1%Fe in solution. The formation of two liquid layers and the occurrence of a crystallisation interval are not observed.

The transformations in the solid state have been examined by the differential method, and it is found that the sulphide is without influence on the transformation points of iron. A polymorphic transformation of ferrous sulphide occurs at 298°, and has been studied by the dilatometric method, using mercury as the filling liquid. The transformation at 138° is also observed in all mixtures containing more than 7% Fe (compare Rinne and Boeke, A., 1907, ii, 471). The brittleness of iron containing sulphide is due to this transformation.

Photo-micrographs of the alloys are given. The eutectic tends to become segregated in mixtures rich in sulphide. Alloys which have been in contact with oxygen contain a new eutectic. Fusion of iron sulphide with iron oxide, however, leads to the elimination of sulphur and formation of ferrite, and the structure is better developed by fusing the sulphide in contact with air. The composition of the eutectic is uncertain. The brittleness of iron containing sulphur at a red heat is due to the absorption of oxygen in this form.
                                        C. H. D.

Stability of the Oxides of Cobalt in the Interval from Co_2O_3 to CoO. SIEOFRIED BURGSTALLER (*Chem. Zentr.*, 1912, ii, 1525—1526 ; from *Abhandl. Deut. naturwiss.-med. Ver. Böhmen*, 1912, 3, 83—143).— The stability of the oxide of cobalt has been followed dynamically, in view of the numerous oxides mentioned in the literature and of the statical measurements of the dissociation pressures made by Richards and Baxter (A., 1900, ii, 78) and by Smith and Foote (A., 1908, ii, 847).

By means of baths of diphenylamine, b. p. $301 \cdot 9°/760$ mm., anthra-cene, b. p. $339 \cdot 8°/760$ mm., and anthraquinone, b. p. $377 \cdot 2°/760$ mm. the dissociation temperature of cobaltic oxide has been narrowed down to $372—373°/760$ mm. Above this temperature the reduction of the oxide has been followed in a sulphur bath and in an electric oven, and after allowing for the possible sources of error (such as the time taken in warming up and in cooling down), the alteration of the oxygen concentration of the oxide with time, by rising or falling temperature, has been graphically portrayed.

From the dissociation temperature of cobalic oxide to a point between $705 \cdot 5°$ and $869°$, cobalto-cobaltic oxide is stable, above which the region for cobaltous oxide occurs. The transition points cannot be determined, however, because regions of solid solution of one oxide in the other must be passed through. From the reactions curve of the oxidation of cobalt in air it is also seen that between $300°$ and $431°$, cobalto-cobaltic oxide is formed, and that at $869°$ the region of solid, solution between Co_3O_4 and CoO is entered.

The existence of solid solutions, and the fact that the speed of the dissociation becomes very slow after a short time, explain the numerous references to improbable oxides of cobalt. J. C. W.

The Replacement of Metals from Aqueous Solutions of their Salts by Hydrogen at High Temperatures and Pressures. IV. VLADIMIR IPATIEV and B. ZRJAGIN (*Ber.*, 1912, 45, 3226—3229. Compare A., 1912, ii, 50).—In solutions of $2N$- and $0 \cdot 2N$-cobalt sulphate and initial pressures of 100 atmos. of hydrogen, no formation of a precipitate takes place within twenty-four hours at $103°$. At $145—150°$ a rosy-violet coloured, crystalline precipitate is formed, having the composition $CoSO_4,H_2O$; metallic cobalt also separates. If nitrogen or air is used instead of hydrogen, the $2N$-solution gives only the salt $CoSO_4,H_2O$.

When a quartz tube is used instead of a glass one, the reaction is not complete at $150°$ within four days, cobalt sulphate still remaining in solution. A glass tube could not be used for so long a time without being attacked.

At $150°$, $2N$- and $0 \cdot 2N$-cobalt nitrate solutions behave similarly to the sulphate solutions at $103°$. At $205—210°$ a crystalline, brownish-black precipitate of cobaltic oxide, which is contaminated with silicic acid from the glass tube, is formed within a day (compare nickel nitrate, A., 1912, ii, 51). A similar result is obtained with N-solutions, both in glass and quartz tubes, whereas N-solutions of nickel nitrate give a small quantity only of a green, crystalline precipitate, containing $52 \cdot 90—53 \cdot 36\%$ of nickel.

Solutions of cobalt chloride behave similarly to those of nickel chloride (*loc. cit.*), the reaction being reversible, namely, $CoCl_2 + H_2 \rightleftharpoons Co + 2HCl$.

T. S. P.

The Origin of the Colour Produced by Cobalt Solutions in Certain Mineral Colours. Siegfried Burgstaller (*Chem. Zentr.*, 1912, ii, 1523—1525; from *Abhandl. Deut. naturwiss.-med. Ver. Böhmen*, 1912, **3**, 57—80).—The coloured residues obtained by moistening certain inorganic oxides with cobalt solutions and then igniting are shown to be solid solutions in which a white substratum, such as alumina, does not modify the blue or red colour of the cobalt ion, whereas a yellow oxide, such as hot zinc oxide, produces a mixed colour.

Rinmann's green, prepared at 750—760° from zinc oxide moistened with cobalt nitrate, was extracted with ammonium carbonate, in which a solid solution of 7·05 mol. CoO to 100 mol. ZnO dissolved, whereas free cobaltous oxide was insoluble. Thénard's blue, obtained by evaporating aluminium nitrate with cobalt nitrate solution, and igniting the residue, also contained cobaltous oxide. No solvents could be found which would separate the solid solution from the free oxide, and other methods for investigating its constitution are being pursued.

J. C. W.

Ternary Alloys of Nickel-Manganese-Copper. Nicola Parravano (*Gazzetta*, 1912, **42**, ii, 385—394).—The paper contains an account of this ternary system derived from the results of its thermal analysis and from the thermal analysis of the three constituent binary systems. Of these, the system Ni-Mn has been previously described by the author (A., 1912, ii, 1175), and the remaining two by other writers. The results of some new experiments with the system Cu-Mn are also given. The nature of the ternary system is exhibited in diagrams, and photographs are reproduced of a number of the ternary alloys prepared.

R. V. S.

The Constitution of the Halogen Compounds of Bivalent Molybdenum. Ivan Koppel (*Zeitsch. anorg. Chem.*, 1912, **77**, 289—300).—The compounds having the empirical composition $MoCl_2$ and $MoBr_2$ are known to react in a manner which indicates a more complex constitution. The properties are now reviewed, and constitutional formulæ are proposed. The most important properties are the existence and stability of the radicles $(Mo_3R_4)''$, the formation of a crystalline hydroxide, the resistance to oxidation, the difference in solubility between the anhydrides and the hydrates, and the amphoteric character of the radicles.

The formulæ given assume a co-ordination number 4, the insoluble hydrates, for example, being $[Mo_3Cl_4R_2, 2H_2O]H_2O$, where R is a halogen. The amphoteric hydroxy-compound is represented as $[Mo_3Cl_4(OH)_2, 2H_2O]$, and the formation of salts from it is necessarily accompanied by isomeric change.

C. H. D.

Molybdates. Georg Wempe (*Zeitsch. anorg. Chem.*, 1912, **78**, 298—326).—Ammonium tetramolybdate is best obtained by the

 action of warm hydrochloric acid on the ordinary molybdate, and forms transparent, triclinic crystals, $(NH_4)_2O,4MoO_3,2H_2O$, of which 3·67 grams dissolve in 100 c.c. of water at 18°. Further decomposition gives the trimolybdate, $(NH_4)_2O,3MoO_3,H_2O$. Sodium tetramolybdate, $Na_2O,4MoO_3,6H_2O$, obtained by the action of nitric acid on the ordinary salt, is much more soluble than the ammonium salt. The trimolybdate is obtained with 6 or 9 H_2O from the mother liquor. Potassium tetramolybdate has not been obtained, the corresponding solutions yielding instead the trimolybdate, $K_2O,3MoO_3,3H_2O$. The potassium hydrogen tetramolybdate has the composition
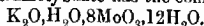
$$K_2O,H_2O,8MoO_3,12H_2O.$$

Lithium tetramolybdate, obtained from Rammelsberg's salt and hydrochloric acid, forms triclinic crystals, $Li_2O,3H_2O,16MoO_3,6·5H_2O$, from which a trimolybdate is obtained with 2 or 4 H_2O. A second tetramolybdate is $Li_2O,H_2O,8MoO_3,10H_2O$. The *rubidium* tetramolybates obtained are $Rb_2O,4MoO_3$; $Rb_2O,H_2O,8MoO_3,3H_2O$; $Rb_2O,MoO_3,Rb_2O,3MoO_3,5H_2O$; and $Rb_2O,4MoO_3,4H_2O$, whilst the trimolybdate has been obtained with $3H_2O$. The *caesium* salts are $Cs_2O,4MoO_3,3H_2O$; $5Cs_2O,12MoO_3,11H_2O$; and

$$Cs_2O,MoO_3,Cs_2O,3MoO_3,4·5H_2O.$$
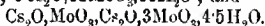
The *calcium*, $CaO,2H_2O,12MoO_3,21H_2O$ and $CaO,H_2O,8MoO_3,16H_2O$; *barium*, $BaO,H_2O,8MoO_3,14H_2O$ and $2(BaO,4MoO_3),7H_2O$; *strontium*, $2SrO,3H_2O,20MoO_3,21H_2O$; *thallous*, $Tl_2O,4MoO_3,H_2O$; *silver*, $Ag_2O,4MoO_3,6H_2O$; *cadmium*, $CdO,H_2O,8MoO_3,6H_2O$; *magnesium*, $MgO,H_2O,8MoO_3,20H_2O$; and *zinc*, $ZnO,H_2O,8MoO_3,14H_2O$, salts have also been obtained. C. H. D.

Iso· and Hetero-poly-acids. VI. Hydrates of Some Hetero-poly-acids. ARTHUR ROSENHEIM and JOHANNES JAENICKE (*Zeitsch. anorg. Chem.*, 1912, 77, 239—251. Compare A., 1911, i, 109, 265; ii, 116, 612).—The following new hydrates of 12-phospho-tungstic acid have been prepared: $H_7[P(W_2O_7)_6],28H_2O$, which is metastable at the ordinary temperature, and passes into the stable 22-hydrate. The transformation point must be below 0°. The addition of concentrated nitric acid to the solutions of precipitates the 19-hydrate.

12-Silicotungstic acid also yields two new hydrates,
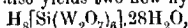
$$H_8[Si(W_2O_7)_6],28H_2O,$$

which is stable below 29°, and the 22-hydrate, which is stable between 29° and 53°. 12-Borotungstic acid forms $H_9[B(W_2O_7)_6],28H_2O$, which does not pass into a 22-hydrate when heated. Nitric acid precipitates a 10-hydrate. The 22-hydrate previously described is hexagonal, and is derived from an acid isomeric with that of the 28-hydrate, the two hydrates crystallising simultaneously from solution.

Metatungstic acid, which is also a 12-hetero-poly-acid, yields only a single hydrate, $H_{10}[H_2(W_2O_7)_6],23H_2O$. 12-Phosphomolybdic acid yields a 28-hydrate, $H_7[P(Mo_2O_7)_6],28H_2O$, which apparently yields a 12-hydrate on dehydration, but the individual character of this hydrate is uncertain. A 22-hydrate is obtained by precipitation with nitric acid.

12-Silicomolybdic acid also forms a $H_8[Si(Mo_2O_7)_6],28H_2O$, from

which nitric acid precipitates a 12-hydrate, but a 22-hydrate has not been obtained.   C. H. D.

Action of Acids on Uranous Oxide. A. COLANI (*Compt. rend.*, 1912, **155**, 1249—1251).—Using uranous oxide prepared by reduction of the green oxide with hydrogen, the author has obtained results widely different from those of Raynaud (A., 1912, ii, 166, 948). Whilst but a small amount of the uranous oxide goes into solution with sulphuric acid, a considerable amount is converted into the sulphate, and as such remains in the insoluble portion. Uranous oxide only dissolves slowly in hydrochloric acid, the amount dissolved in a given time varying widely with the mode of preparation of the oxide. Solution is continuous over a very long period of time.   W. G.

Asserted Explosibility of Uranyl Nitrate. LAUNCELOT W. ANDREWS (*J. Amer. Chem. Soc.*, 1912, **34**, 1686—1687 ; *Chem. Zeit.*, 1912, **36**, 1463).—With reference to the statement of Ivanov (A., 1912, ii, 455) on the explosibility of uranyl nitrate, the author records the explosion of a quantity of uranyl nitrate, in the preparation of which ether had been employed. On adding strong solution of potassium hydroxide to some of the salt which had escaped decomposition, a marked odour of ether was produced, whilst another specimen when dissolved in water gave a deep blue colour to Congo-red paper, indicating the presence of nitric acid. It is considered that in this case the explosion was due to the water of crystallisation of the uranyl nitrate, $UrO_2(NO_3)_2,6H_2O$, having been replaced by ether and nitric acid, and it is regarded as probable that Ivanov's explosion was due to the same cause.   E. G.

The System Tin-Iodine. WILLEM REINDERS and S. DE LANGE (*Proc. K. Akad. Wetensch.·Amsterdam*, 1912, **15**, 474—481*).—The freezing-point curve for mixtures of iodine and stannic iodide consists of two branches meeting at a point corresponding with 79·6° and 60% by weight of stannic iodide. The corresponding boiling-point curve, which has been determined for atmospheric pressure, shows neither maximum nor minimum.

When stannic and stannous iodide are heated together at 350°, two liquid layers are formed, one of which consists of almost pure stannic iodide, whilst the other layer represents stannous iodide together with at most 6% of stannic iodide. When iodine is melted in contact with a small excess of tin, the product first formed is almost exclusively stannic iodide. The reaction $SnI_4 + Sn = 2SnI_2$ takes place extremely slowly, and even at 350° the velocity of this change is comparatively small.

Pure stannic iodide melts at 143·5° and boils at 340°, the corresponding temperatures for the stannous salt being 320° and 720°.
                                                  H. M. D.

The Volatisation of Vanadic Acid by Halogens. ERNST B. AUERBACH and K. LANGE (*Zeitsch. angew. Chem.*, 1912, **25**, 2522—2523). —The observation of Ephraim (A., 1903, ii, 487) that vanadic acid

* and *Zeitsch. anorg. Chem.*, 1912, **79**, 230—238.

volatilises with hydrochloric acid, is confirmed. The loss when vanadic acid is heated with sodium chloride is also appreciable. When barium chloride is used, it is found that the greater part of the chlorine may be driven off with very little loss of vanadium, the chloride first formed being decomposed by the atmospheric moisture. If heated in a stream of dry carbon dioxide, red vapours are obtained, which condense to an oily liquid of unknown composition, containing vanadium. It is necessary, in the estimation of vanadium by means of mercurous nitrate, that chlorides should be absent. C. H. D.

Hetero-poly-acids Containing Vanadic Acid. WILHELM PRANDTL (*Zeitsch. anorg. Chem.*, 1912, 79, 97—124. Compare A., 1912, ii, 167).—The author's view that compounds of this kind are derived from a hexa-vanadic acid is contrasted with the formulation due to Miolati (A., 1908, ii, 595) and Rosenheim (A., 1911, i, 109, 265; ii, 116, 612; this vol., ii, 59). Most of the well-defined compounds of this class may be represented as additive compounds of 4 or 6 mols. of molybdate and 1 mol. of hexavanadate.

Ammonium paramolybdate, $3(NH_4)_2O,7MoO_3,4H_2O$, is regarded as a compound of 1 mol. of diammonium trimolybdate with 4 mols. of ammonium hydrogen molybdate, $(NH_4)_2H_4Mo_3O_{10},4NH_4HMoO_4$. Acids remove ammonia from the monomolybdate molecule, which then polymerises to the trimolybdate, from which the hexamolybdate is obtained by elimination of water.

[With SIOMUND PERKOWSKI.]—The following new salts have been obtained: $KVO_3,K_2MoO_4,4H_2O$, or $K_3V_3O_9,3K_2MoO_4,12H_2O$, the normal salt of the series, which is pale yellow and very sensitive to acids. $Na_4V_6O_{17},6NaHMoO_4,12H_2O$, also yellow.
$$Na_6V_6O_{18},6Na_2H_4Mo_3O_{12},36H_2O,$$
pale yellow. $Ba_3V_6O_{18},6Na_2H_4Mo_3O_{12},20H_2O$ or $74H_2O$, according to the conditions of precipitation.
$$Na_2H_2V_6O_{17},Na_2H_4Mo_3O_{12},4NaHMoO_4,16H_2O ;$$
$K_2HV_6O_{17},2KHMoO_4,2K_2H_4Mo_3O_{12},6H_2O$, which are more deeply coloured. $(NH_4)_4V_6O_{17},2NH_4HMoO_4,2(NH_4)_2H_4Mo_3O_{12},8H_2O ;$
$(NH_4)_3HV_6O_{17},2(NH_4)_2H_4Mo_3O_{12},4NH_4HMoO_4,6H_2O.$
These salts are tabulated and correlated with others of the same series described in the literature. C. H. D.

Chemical Reactions of β-Gold and Crystallised Gold. MAURICE HANRIOT and FRANÇOIS RAOULT (*Compt. rend.*, 1912, 155, 1085—1088. Compare A., 1911, ii, 791).—Contrary to general belief, ordinary gold as well as the brown (β) modification is attacked by nitric acid, the amount dissolved, whilst small, varying with the concentration of the acid, the β-modification being readily acted on. Fuming hydrochloric acid in the presence of oxygen also has a marked solvent effect. The best solvent for β-gold is a hot solution of auric chloride containing hydrochloric acid. On cooling the solution the dissolved gold crystallises out in the metallic state, and a determination of its magnetisation coefficient shows that, in this form, it consists almost entirely of the β-variety. This solvent has a much more marked action on the brown than the yellow gold, and it is the β-variety which passes into solution, thus leaving the insoluble residue

enriched with the a-variety. This fact is borne out by comparison of the magnetisation coefficients of the original brown gold, the crystallised gold, and the insoluble residue.   W. G.

The Preparation and Application of Colloidal Platinum Metale. ALADAR SKITA and W. A. MEYER (*Ber.*, 1912, 45, 3579—3589).—See this vol., i, 53.

Osmium Tetroxide as an Oxygen-carrier and the Activation of Chlorate Solutions. KARL A. HOFMANN (*Ber.*, 1912, 45, 3329—3336).—In the presence of about 1 mg. of osmium tetroxide per 500 c.c., 1% solutions of *p*-leucaniline and leucomalachite-green become strongly coloured after a few hours on shaking in the presence of air.

Under an oxygen pressure of 10 atmospheres and temperatures of 50—100°, the following oxidations take place in the presence of 0·01 gram of osmium tetroxide per 200 c.c. of liquid: 40% alcohol is oxidised in three to four hours to acetic acid and aldehyde or acetal, traces of crotonaldehyde also being formed ; 50% methyl alcohol gives formaldehyde and formic acid. The action on the aldehydes takes place very slowly, or not at all ; for example, paracetaldehyde and acetal shows no signs of oxidation within eight days at 20° ; vanillin only after twenty-four hours.

The acids, formic, acetic and oxalic, are very stable towards osmium tetroxide. Aniline sulphate is readily oxidised, and anthracene gives anthraquinone in acetic acid solution.

The following oxidising actions of potassium chlorate, in neutral or slightly acid solutions, take place very readily in the presence of osmium tetroxide, but not at all, or only extremely slowly, in its absence: arsenic to arsenic acid, hypophosphorous acid to phosphoric acid ; hydrazine sulphate quantitatively to nitrogen, indigo-carmin to indigo-white, quinol to quinhydrone, aniline to emeraldin ; mono- and di-methylaniline are oxidised ; benzidine to diphenoquinone-di-imide, *p*-leucaniline and leucomalachite-green to the dyes ; catechol, resorcinol, and tannin are oxidised, anthracene to anthraquinone, ethyl alcohol to acetal, no chlorination taking place ; slightly acid potassium formate to carbon dioxide. Substances containing the ethylene linking, such as ethylene, propylene, amylene, indene, *r*-pinene, and dichloroethylene, CHCl:CHCl, are readily oxidised ; trichloroethylene, CHCl:CCl$_2$, is only slowly oxidised, and perchloroethylene not at all. Allyl alcohol is much more readily oxidised than ethyl alcohol ; *iso*eugenol is readily oxidised, whilst vanillin is not. Benzene containing thiophen gives a reaction due to the presence of the thiophen. Acetylene is oxidised.

Benzoic acid, bromobenzoic acid, naphthalene, and saturated ketones are not affected, and benzaldehyde only very slowly.   T. S. P.

Mineralogical Chemistry.

Origin of Native Sulphur. A. W. Kruemmer and R. Ewald *(Centr. Min.,* 1912, 638—640).—A large cavity in gypsum met with in the Barsinghausen mines was lined with bitumen, resting on which were large crystals of sulphur. Between the gypsum and the bitumen was a zone of calcium carbonate; and the gases in the cavity contained hydrogen sulphide and hydrocarbons. The sulphur had no doubt been formed by the reducing action of the hydrocarbons on the gypsum, for example:

I. $CaSO_4 + CH_4 = CaS + CO_2 + 2H_2O = CaCO_3 + H_2S + H_2O.$
II. $H_2S + H_2O + O = 2H_2O + S.$
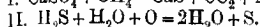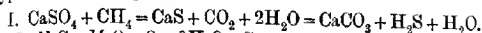
The deposits of sulphur in Sicily, which are associated with gypsum and outbursts of gas containing hydrocarbons and carbon dioxide, have probably been formed in a similar manner. L. J. S.

Asphalt Theory of the Formation of Naphtha. K. W. Charitschkov *(Chem. Zeit.,* 1912, **36**, 1402).—The author finds that the decomposition products of Russian asphalt exhibit similarity to many Russian mineral oils. Specimens of the former yield, when distilled, paraffins, oils, and residues analogous to, and in approximately the same amounts as, the mineral oils, as shown in the appended table:

B. p.	Decomposition product.	Mineral oil (Grosny).
to 110°	5·72% (D 0·720)	4·78% (D 0·705)
110—150°	10·63% (D 0·765)	10·45% (D 0·7443)
150—220°	26·5 % (D 0·8108)	16·2 % (D 0·7219)

The author is led to the conclusion that naphtha is a product of the decomposition of asphalt. H. W.

Vrbaite, a New Thallium Mineral from Allchar, Macedonia. B. Ježek *(Zeitsch. Kryst. Min.,* 1912, **51**, 364—378). Chemical Examination of Vrbaite. Fr. Křehlík *(Ibid.,* 379—383).—The new mineral was found as small (about 1 mm.) crystals embedded in realgar and orpiment. The crystals are orthorhombic, $a : b : c = 0·5659 : 1 : 0·4836$, with a tabular or pyramidal habit and a good brachypinacoidal cleavage. The mineral is opaque with a metallic to semi-metallic lustre and a greyish-black colour, but in thin splinters it is dark red and translucent; the streak is bright red with a tinge of yellow. $H = 3\frac{1}{2}$, D 5·30. It is readily fusible before the blowpipe, and is easily soluble in nitric acid. Analysis gives the formula $TlAs_2SbS_5$, representing a thallous salt of the acid HAs_3S_5, in which one atom of arsenic is replaced by antimony:

Tl.	Sb.	As.	S.	Fe.	Total.
29·52	18·34	24·06	25·20	1·85	98·97

L. J. S.

Iron Sulphide in the Miocene Clays of Govt. Samara, Russia. Bruno Doss (*Jahrb. Min.*, 1912, *Beil.-Bd.* 33, 662—713). —In boring for artesian water on the estates of the Brothers Melnikov, in the Novo-Usensk district, outbreaks of natural gas, containing 67·65% CH_4, 20·70% N, were encountered. The clays in these borings are impregnated with a black, very finely divided iron sulphide, which differs from the hydrated iron sulphide met with in the black mud of lakes and ponds. The material is magnetic; D 3·57—4·16 (the true value being probably 4·2—4·3). Analysis gave: Fe, 46·24; S, 51·92; insoluble, 3·95%, corresponding with the formula FeS_2. In another analysis the figures correspond with Fe_5S_7. The material is soluble in cold dilute hydrochloric acid with evolution of hydrogen sulphide, and it is much more readily attacked by various reagents (potassium cyanide, potassium hydroxide, iodine solution, etc., and even by boiling water) than is iron-pyrites. The material is regarded as a labile phase of iron disulphide, and is named *melnikovite*. Its mode of origin is discussed; it is regarded as having been derived from a colloidal form of iron sulphide.   L. J. S.

Bauxite of the Croatian Karst and its Origin. Mijat Kišpatić (*Jahrb. Min.*, 1912, *Beil.-Bd.* 34, 513—552).—Twenty analyses are given of bauxite from various localities in Croatia and also in Dalamatia and Bosnia; the extreme values shown are quoted under I and II. Analysis III is of the bauxite ("wochenite") from Wochein, Carniola:

	SiO_2.	TiO_2.	ZrO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	Ign.	Total.
I.	0·87	nil.	nil.	24·54	1·80	nil.	nil.	8·11	—
II.	33·00	8·51	2·71	66·68	26·89	1·21	6·79	19·97	—
III.	61·31	trace	trace	16·95	12·46	trace	—	6·40	99·75

At these localities the bauxite occurs as beds in limestone and dolomite; it is dull red in colour, and usually oolitic in structure. Microscopical examination shows that the main constituent has the form of minute isotropic granules; this material is named *sporogelite* (compare Tućan, this vol., ii, 69), and to it is assigned the composition Al_2O_3,H_2O, corresponding with the crystalline diaspore. This colloidal material is sometimes white, but usually it is coloured by intermixture with colloidal iron oxide and hydroxide. Other minerals present, although usually only in small amounts, include diaspore, hydrargillite, quartz, felspar, amphiboles, felspars, micas, epidote, rutile, zircon, etc. The same materials were obtained when the limestones and dolomites were dissolved in acid; and it is considered that these bauxites, as well as those from some other localities (France, Italy, Georgia, etc.), represent the insoluble residues resulting from the weathering of these rocks. On the other hand, certain other bauxites (from the Vogelsberg) and laterite are the products of decomposition of basalt and other silicate rocks.   L. J. S.

A New Deposit of Chrome-iron-ore in Northern Caucasus. N. Besborodko (*Jahrb. Min.*, 1912; *Beil.-Bd.*, 34, 783).—Veins of compact to granular chrome-iron-ore have been discovered in serpentine

about 12 km. south of the village Psemjonowka in prov. Kuban. Analysis I of an ore'sample corresponds with about 85% of chromite. Secondary minerals occurring in the serpentine (an altered olivine-rock) include chrysotile, antigorite, chrome-chlorites (kaemmererite and kotschuheite), revdinskite, carbonates, and quartz. The revdinskite (anal. II) is apple-green with brownish patches, and occurs sparingly as a thin coating on the serpentine.

	SiO$_2$.	Cr$_2$O$_3$.	Al$_2$O$_3$.	FeO.	NiO.	MnO.	MgO.	CaO.	H$_2$O.	Total.
I.	1·66	59·09	8·08	18·43	—	0·20	12·47	0·91	0·20	101·04
II.	20·5	—	22·0		6·2	—	29·9	—	23·4	102·0

In the same district chromium and nickel minerals, respectively fuchsite and millerite, were detected in a contact-metamorphic rock (silicate hornfels).   L. J. S.

Carboniferous Limestones of the Avon Gorge, Bristol. MILDRED B. CHAPMAN (*Geol. Mag.*, 1912, [v], 9, 498—503).—Twenty-one analyses are given of limestones from the various fossiliferous zones. The extreme values are: CaO, 29·38—55·63%; MgO, 0—16·76%; CO$_2$, 24·62—44·72%; Fe$_2$O$_3$ + Al$_2$O$_3$, 0·08—5·87%; insoluble in hydrochloric acid, 0·02—43·29%; P$_2$O$_5$, 0—0·14%. The insoluble residue consists of quartz, black carbonaceous matter, chalcedony, weathered felspar, zircon, and tourmaline. Those limestones which have been formed under coral-reef conditions contain very variable amounts of insoluble residue, whilst those which were rapidly deposited near a coastline are more pure.   L. J. S.

Tsumebite, a New Lead Copper Phosphate. KARL BUSZ (*Festschrift Deut. Naturf. Aertze, Münster*, 1912, 182—185).—The new mineral occurs as small, emerald-green crystals with cerussite and chessylite on snow-white calamine (ZnCO$_3$), the latter cementing fragments of reddish-brown dolomite in the mines at Tsumeb, Otavi, German South-West Africa. The crystals are monoclinic with $a:b:c = 0·9974:1:0·8215$; $\beta = 81°44'$. Analysis agrees with the formula P$_2$O$_5$,5(Pb,Cu)O,8H$_2$O:

PbO.	CuO.	P$_2$O$_5$.	H$_2$O.	Total.	Sp. gr.
63·77	11·79	12·01	12·33	99·90	6·133

L. J. S.

Ludlamite from Ashio, Japan. NOBUYO FUKUCHI (*Beitr. Min. Japan*, 1912, No. 4, 192—194).—This iron phosphate is found in the Ashio copper mines, prov. Shimotsuke, as druses of light green, transparent crystals, with a bright vitreous lustre. It is associated with crystals of vivianite, and it sometimes forms pseudomorphs after vivianite. The crystals are monoclinic and have the form of thick six-sided tablets with a perfect basal cleavage. H = 3½; streak, white. Analyses give the formula Fe$_7$(OH)$_2$(PO$_4$)$_4$,7H$_2$O:

FeO.	P$_2$O$_5$.	H$_2$O.	Insol. (in HCl).	MnO,Al$_2$O$_3$,CaO,MgO.
53·21	32·03	14·60	trace	traces
50·54	31·38	13·79	3·67	—

L. J. S.

The Constitution of Some "Salic" Silicates. HENRY S. WASHINGTON (*Amer. J. Sci.*, 1912, [iv], **34**, 555—571).—Accepting Streng's and Groth's suggestion that the quinquevalent groups $(R'Si)^v$ and $(R''Al)^v$, and in some cases the decivalent group $(CaSi_2)^x$, are present in certain silicates, the author shows that the constitution of all the members of the felspar, leucite, nephelite, and scapolite groups, and nearly all the zeolites, can be interpreted in such a way as to explain readily their composition, mutual relations, poly- and iso-morphism, resistance to acids, and their relation to the mutually common end alteration product, kaolinite.

The felspars, lenads (felspathoids, including leucite, nephelite, and their congeners), and most zeolites are regarded as salts, or isomorphous mixtures of salts, of an alumino-silicic acid, $H_5AlSi_2O_8$, or most probably of a polymeride of this, the five hydrogen atoms being isomorphously replaced by the groups $(R'Si)^v$, $(R''Al)^v$, and $(R''Si_2)^x$, R' being K, Na and Li, and R'' being Na_2, K_2, Ca, and rarely Ba and Sr.

The scapolites are interpreted as salts of a different alumino-silicic acid, $H_{10}AlSi_3O_{12}$, the hydrogens being entirely replaced by the radicles $(NaSi)_2$ and $(CaAl)_2$. T. S. P.

Sinter from the Geyser of Obama, Japan. DENZŌ SATŌ (*Beitr. Min. Japan*, 1912, No. 4, 139—141).—The water issuing from the hot springs of Obama, prov. Hizen, is clear and odourless, with a slightly alkaline reaction, and a temperature of $100°$. Three analyses of water from different springs are given: that from the Funtō-yu contains per litre: $CaCO_3$, 0·32150; $FeCO_3$, 0·01626; Na_2SO_4, 0·63577; NaCl, 5·66341; KCl, 1·63388; $MgCl_2$, 0·53581; $CaCl_2$, 0·27539; SiO_2, 0·21800; total solids 9·20390. $D^{15.5}$ 1·006. Analysis of a snow-white incoherent sinter forming a small cone around the orifice of this spring gave:

SiO_2.	Fe_2O_3.	Al_2O_3.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	CO_2.	Cl.	Ign.	Total.
16·59	0·41	0·18	1·80	38·23	7·28	0·20	0·89	23·23	1·03	10·46	100·40

L. J. S.

A Felspar of Porto-Scuso (Sardaigne). GIUSEPPE CESARO (*Bull. Acad. roy. Belg.*, 1912, 553—569).—A detailed account of the crystallographic examination of a felspar from Porto-Scuso, which analysis shows to be a sodium orthose, with two molecules of sodium oxide and one of potassium oxide. The numerical data are tabulated. The author discusses the effect of the replacement of potassium by sodium on the values of the fundamental angles, and from his results calculates the values of these angles for a purely sodium orthose. At the end of the paper he gives an account of a method for measuring, under the microscope, the angle of the optical axes in a section passing through the obtuse bisectrix, and inclined to the acute bisectrix. The error for the method is calculated, that for 2ψ being 30′, that relative to a being 2′; for $2V$ 22′ to 24′. W. G.

Sericite from North Wales: Penninite and Labradorite from Ireland. ARTHUR HUTCHINSON and WALTER CAMPBELL SMITH (*Min. Mag.*, 1912, **16**, 264—271).—Sericite (anal. 1) occurs as talc-like

aggregates of pale-green flakes in quartz veins intersecting dolerite and slate at Tan-y-Bwlch, Merionethshire. Refractive indices, $\beta = 1.589$, $\gamma = 1.594$, $2E = 68°50'$. In composition it conforms with type I of Clarke's formula, $Al(SiO_4)_3Al_2R_3'$. Penninite (anal. II) forms colourless to pale brown, hexagonal plates in the ophicalcite ("Connemara marble") which is quarried at Recess, Co. Galway. In composition, $H_{93}Mg_{12}Al_5Si_9O_{49}$, it approximates to pseudophite. Labradorite (anal. III) occurs as large, porphyritic crystals in dolerite dykes at St. John's Point near Ardglass, Co. Down. The optical constants are: $\alpha = 1.5630$, $\beta = 1.5665$, $\gamma = 1.5712$, $2V = 81°48'$, extinction on $(001) - 11°$, on $(010) - 23°$; angle $(001):(010) = 85°57'$. Formula,

$$33NaAlSi_3O_8,5KAlSi_3O_8,62CaAl_2Si_2O_8.$$

	SiO₂	Al₂O₃	Fe₂O₃	FeO	CaO	MgO	K₂O	Na₂O	H₂O. (>105°).	H₂O. (105°).	Total.	Sp.gr.
I.	46·51	36·58	0·51	0·48	0·44	0·46	7·84	1·77	5·03	0·11	99·73	2·798
II.	34·81	16·21	1·09	0·36	0·75	30·05	1·85	—	12·71	1·89	99·72	2·619
III.	52·33	30·22	0·40	—	12·52	—	0·85	3·62	0·36		100·30	2·706

<div align="right">L. J. S.</div>

Laumontite from Ashio, Japan. NOBUYO FUKUCHI (*Beitr. Min. Japan*, 1912, No. 4, 190—192).—A vein of laumonite occurs in liparite, the country-rock of the Ashio copper mines, prov. Shimotsuke. Crystals are perfectly colourless and long-prismatic in habit. Analysis of the fresh crystals gave the following results, corresponding with the formula $H_4CaAl_2Si_4O_{14},2\frac{1}{2}H_2O$; other determinations of water varied from 16·02 to 16·43%.

SiO₂.	Al₂O₃.	CaO.	H₂O.	Na₂O,K₂O,MgO, etc.
50·79	18·49	10·69	16·20	3·83

On exposure to the air, the crystals soon fall to a white powder, in which was found only 14·44% water, corresponding with the formula $H_4CaAl_2Si_4O_{14},2H_2O$. The latter formula is the one usually given for laumontite. L. J. S.

Minerals of Taiwan (=Formosa). YŌHACHIRŌ OKAMOTO (*Beitr. Min. Japan*, 1912, No. 4, 157—188).—Fifty-one species of minerals (including petroleum and coal) are described; analyses are given of the following. Hornblende, as black crystals in the hornblende-pyroxene-andesite of the Daiton volcanic group (anal. I and II). Fuller's earth (?), white, greyish-blue or yellow, and more or less greasy, from Hōko-tō (anal. III); hygroscopic water 10·50%; portion soluble in hydrochloric acid 64·96%.

	SiO₂.	Al₂O₃.	Fe₂O₃.	FeO.	MnO.	CaO.	MgO.	Na₂O.	K₂O.	Ign.
I.	43·99	15·04	13·75	—	0·52	10·55	11·35	0·34	0·19	3·44
II.	41·67	14·14	—	16·18	0·69	11·10	14·16	1·98		nil.
III.	56·06	19·72	11·35	—	—	—	2·25	not det.		—

Alunite occurring as crystals (up to 2 cm. across) with auriferous enargite and native sulphur in the Kinkwaseki gold mines; IV. of pale violet and V of white alunite.

	SO₃.	Al₂O₃.	Fe₂O₃.	MgO.	K₂O.	H₂O.	Insol.	Total.	Sp. gr.
IV.	34·90	37·40	trace	nil.	6·18	13·24	7·42	99·14	2·787
V.	38·65	35·88	,,	0·69	6·09	11·60	6·42	99·33	—

A radioactive mineral consisting of barium and lead sulphate is deposited, together with native sulphur, etc., .hy the Hokuto hot springs, in the Daiton volcanic group. The water has a strong acid taste (containing free hydrochloric acid), an odour of hydrogen sulphide, and a temperature of 80—90°; it contains in 1000 parts: Na_2SO_4, 1·9055; NaCl, 0·9990; $Al_2(SO_4)_3$, 0·6588; KCl, 0·7130; NH_4Cl, 0·6073; $CaSO_4$, 0·4787; $FeSO_4$, trace; $Fe_2(SO_4)_3$, 0·5420; $MgSO_4$, 0·2024; $Al_2(HPO_4)_3$, 0·0012; $BaSO_4$, 0·0007; $PbSO_4$, trace; H_2SiO_3, 0·2174; HBO_2, 0·0710; HCl, 1·9596. D_{20}^{36} 1·0150. The radioactive material forms a coarsely fibrous crust (anal. VI) or clusters of brown, rhombic plates (anal. VII). These crystals are zoned and have angles agreeing approximately with those of barytes and anglesite; D 6·1; the α-ray activity is 0·0366 that of uranium oxide. Analysis VIII is of an accompanying dirty-grey crust of siliceous sinter.

	PbO.	BaO.	SrO.	CaO.	SO₃.	Fe₂O₃.	Al₂O₃.	MgO.	K₂O.	Na₂O.	H₂O.	Ign.	P₂O₅.	SiO₂.	Total
VI.	21·96	32·04	0·93	0·51	30·81	3·93	6·88	1·04	nil.	0·53	2·53	—	0·01	1·27	99·44
VII.	19·38	42·27	trace	0·17	31·70	0·43	0·48	0·28	0·14	1·53	—	2·74	nil.	0·97	100·09
VIII*.	—	—	—	0·13	2·48	2·11	2·27	0·30	0·14	0·73	—	14·94	trace	77·10	100·20

* TiO₂ trace.

<div align="right">L. J. S.</div>

The Tourmaline Group. WALDEMAR T. SCHALLER (*Zeitsch. Kryst. Min.*, 1912, **51**, 321—343).—The following determinations of the physical constants and analyses were made on crystals of tourmaline:

	Locality.	Colour.	Sp. gr.	Axis c.	ω.	ε.	ω−ε (Na).
I.	Elba	Pale red	3·05	0·4448	1·651	1·630	0·021
II.	Mesa Grande, California	Red	3·04	0·4479	1·647	1·628	0·019
III.	" " "	Pale green	3·04	0·4489	1·646	1·628	0·018
IV.	Ramona, California......	Black	3·22	0·4534	—	—	—
V.	Lost Valley, California	Black	3·16	—	—	—	—

	SiO₂.	B₂O₃.	Al₂O₃.	Ti₂O₃.	FeO.	MnO.	CaO.	MgO.	K₂O.	Na₂O.	Li₂O.	H₂O.	F.	Total less O for F.
I.	37·89	10·28	43·85	0·04	0·11	0·11	0·07	—	—	2·43	1·66	3·47	0·10	99·85
II.	37·57	10·65	42·18	trace	0·19	0·24	1·20	—	—	2·05	1·92	3·38	0·30	99·09
III.	36·72	10·0	41·27	0·06	1·13	1·48	0·87	—	—	2·23	1·76	3·33	0·31	99·03
IV.	35·21	10·43	36·07	0·23	11·11	0·98	0·25	0·10	—	1·92	trace	3·51	—	99·50
V.	35·96	10·6	33·28	0·36	11·04	0·13	0·42	3·48	—	2·16	—	3·31	—	100·77

These new analyses conform very closely with Penfield and Foote's general formula $H_{20}B_2Si_4O_{21}$ (A., 1899, ii, 304). Together with some earlier analyses, they are discussed in detail. The ratio of $(H_2O + \tfrac{1}{2}F) : SiO_2$ ranges from 3·72 : 12 to 4·17 : 12, and in the special formulæ proposed water is given as $3H_2O$. Further, the alumina varies inversely in amount with the other bases (R = Fe″, Mn″, Ca, Mg, K₂, Na₂, Li₂, and H₂ in excess of the $3H_2O$). The end components as plotted on a curve are:

$$12SiO_2,3B_2O_3,8Al_2O_3,3RO,3H_2O,$$
$$\text{and } 12SiO_2,3B_2O_3,5Al_2O_3,12RO,3H_2O.$$
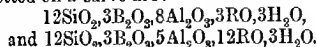
In analysis I of Elba tourmaline still more alumina is present, and the component $12SiO_2,3B_2O_3,9Al_2O_3,3H_2O$ is assumed. There may also be several other members of the series, for example,

$$12SiO_2,3B_2O_3,7Al_2O_3,6RO,3H_2O.$$

Other special types are introduced by replacing RO by MgO, Li₂O, etc.

The composition of Ramona tourmaline (anal. IV) is, for example, expressed by the mixing of the following three components:

$$12SiO_2, 3B_2O_3.8Al_2O_3, 3H_4O, 3H_2O,$$
$$12SiO_2, 3B_2O_3, 7Al_2O_3, 6FeO, 3H_2O,$$
$$12SiO_2, 3B_2O_3, 5Al_2O_3, 12Na_2O, 3H_2O.$$
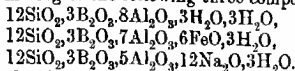
Comparing the chemical composition and the physical constants, it is noticed that the specific gravity, crystallographic axis c, refractive indices, and double refraction reach a maximum with Al_2O_3 35—36%, and that this point separates two series of tourmalines. Magnesia-free-tourmalines contain more, and magnesia-tourmalines less, than this amount of alumina. The former occur in pegmatites, whilst the latter are usually found in metamorphic rocks and are brown or black in colour.　　　　　　　　　　　　　　　　　　　　　　　　　　L. J. S.

Minerals from the Pegmatite of Ampangabé, Madagascar. ALFRED LACROIX (*Bull. Soc. franç. Min.*, 1912, 35, 180—199. Compare A., 1912, ii, 1182).—The pegmatite of Ampangabé, near Miandrarivo, consists of microcline, quartz and muscovite, and is exploited for beryl of gem-quality. This beryl is of the prismatic type very poor in alkalis, D 2·713—2·721. The gem material is of a fine blue colour, but delicate pink, colourless, yellow, and green stones are also found. Other minerals present in the pegmatite include monazite in crystals, columbite crystals, D 5·52 (anal. I by Pisani), ampangabeite (A., 1912, ii, 567), strüverite, etc. The strüverite is found as large, tetragonal crystals (up to 6 kilos.), which are usually elongated in the direction of a pyramid-edge (111 : 111), and sometimes twinned on (101), giving them an orthorhombic aspect. These crystals are optically uniaxial and positive, and have angles very close to the angles of rutile. The material is iron-black with a conchoidal to uneven fracture, D 4·91 ; anal. II by Pisani.

	TiO_2.	Ta_2O_5.	Cb_2O_5.	SnO_2.	FeO.	MnO.	Al_2O_3.	Total.
I.	—	12·60	64·60	0·40	15·00	7·30	—	99·90
II.	71·15	10·14	—	0·05	15·31	—	1·80	98·98

In a beryl-bearing pegmatite from the west of Miandrarivo is a fresh monazite, which in thin flakes is transparent and clear yellow, D 5·11, anal. III by Pisani.

P_2O_5.	Ce_2O_3.	$(La, Di)_2O_3$.	$(Y, Er)_2O_3$.	ThO_2.	Al_2O_3.	Fe_2O_3.	Loss on ignition.	Total.
27·45	31·85	27·90	2·93	9·15	0·21	0·42	0·74	100·65

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Nature and Origin of "Terra rossa." FRAN. TUĆAN (*Jahrb. Min.*, 1912, *Beil.-Bd.* 34, 401—430).—Terra rossa occurs in the crevices and cavities of the bare corroded limestones and dolomites of the Karst district, and it represents the insoluble residue left by the denudation of these rocks. It consists mainly of minute amorphous particles of aluminium hydroxide, Al_2O_3, H_2O ; and for this colloidal mineral (corresponding with the crystalloid diaspore) the name *sporogelite* is proposed. The red colour is due to colloidal ferric hydroxide $(2Fe_2O_3, 3H_2O)$; and various accessory minerals are present as minute grains, namely, quartz, mica, epidote, hydrargillite, diaspore, amphibole, felspar, garnet, rutile, etc. The residues (averaging 0·32%)

obtained by dissolving the limestones in dilute acetic acid, or the dolomites in dilute hydrochloric acid, have the same reddish colour and are identical in mineralogical composition with the terra rossa. Analysis of terra rossa from various localities gave :

	SiO_2.	TiO_2.	ZrO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	$K_2O,Na_2O,$ Li_2O.	H_2O.	CO_2.	Total.
I.	0·37	8·51	0·45	55·37	21·76	trace	trace	trace	trace	13·45	—	99·91
II.	26·20	0·51	0·81	39·14	14·03	1·45	,,	—	,,	18·14*	—	100·28
III.	35·42	0·30	0·10	32·89	15·03	0·93	0·43	trace	,,	15·32	0·23	100·55
IV.	43·61	trace	trace	27·80	11·75	trace	1·64	,,	,,	15·43*	—	100·23
V.	47·89	0·96	,,	24·38	12·63	1·18	0·68	,,	0·32	11·86	0·39	100·29
VI.	46·27	0·80	,,	26·61	12·64	0·12	1·13	,,	trace	13·32*	—	100·89
VII.	26·47	trace	,,	20·19	18·03	1·32	13·19	,,	,,	11·24	9·12	99·56
VIII.	32·11	,,	,,	25·69	6·20	—	14·44	0·48	,,	11·33	10·77	100·97
IX.	66·57	0·12	0·09	21·87	5·72	—	—	—	,,	5·58*	—	99·95

* Loss on ignition.

Analysis I of the purest material, from Županjac, Bosnia, is interpreted as : sporogelite, 70·38%; colloidal ferric hydroxide, 22·025%; rutile, 6·88%; zircon, 0·48%. In the other analyses the silica is present partly as quartz and partly as colloidal silicic acid, the latter being soluble in dilute hydrochloric and nitric acids. In anal. II, for example, 8·99% of the silica is soluble, and represents 43·89% colloidal silicic acid intermixed with 39·54% of sporogelite.

The sporogelite is regarded as an original constituent of the limestones, and to have been precipitated as such from the sea-water at the time that the limestones were deposited. The bauxites of the same region are identical chemically and mineralogically with the terra rossa, but they are of earlier date (compare Kišpatić, this vol., ii, 64).

L. J. S.

Analysis of Red Earth from the Floor of an Ancient Hut. JOHN O. HUGHES (*Chem. News*, 1912, 106, 247).—A reddish-brown earth obtained from the floor of one of the ancient huts forming the stone fortress on the top of Penmaenmawr, Carnarvonshire, was found to have the following composition : substances insoluble in hydrochloric acid, silica, etc., 83·82%; alumina, 2·47%; iron oxide, 4·71%; magnesia, 1·45%; sodium and potassium oxides, 0·52%; phosphoric anhydride, 1·22%; sulphur trioxide, 0·13%; water (at 110°), 1·86%; loss on ignition, 3·70%; manganese oxide, calcium oxide, carbon dioxide, and chlorine, traces. Embedded in the earth were a few small pieces of charcoal. The author is of the opinion that the earth is the ash of some combustible substance (possibly peat) mixed with a portion of the surrounding soil.

W. P. S.

A New Fall of Meteoric Iron in Japan. MASUMI CHIKASHIGÉ and TADASU HIKI (*Zeitsch. anorg. Chem.*, 1912, 77, 197—199).—A meteorite which fell in 1904 at Okano, in the province of Tamba, Japan, has been examined. The meteorite, which weighs 4742 grams, contains Fe, 94·85%; Ni, 4·44%; Co, 0·48%; P, 0·23%; Cu, trace, and has D 7·98. The ground-mass consists of nickeliferous iron, showing Neumann's lines on etching. The phosphide occurs as distinct rhabdite crystals.

Heating at 1300° for thirty minutes causes granulation of the mass, and the Neumann's lines disappear.

C. H. D.

Meteoric Fall near Holbrook, Arizona. GEORGE P. MERRILL (*Smithsonian Miscell. Collections*, 1912, 60, No. 9, 1—4. Compare Foote, A., 1912, ii, 1183).—The stones of this recent and remarkable fall resemble in lithological character those of the Pultusk (Poland) shower of 1868, and in Brezina's classification belong to "spherulitic chondrite, crystalline, Cck." The material consists of orthorhombic with occasional monoclinic pyroxenes and of olivine with small scattered masses of metallic iron and iron sulphide; numerous chondrules are set in a loose aggregate of particles. The iron sulphide forms granules up to 8 mm. across, and resembles pyrrhotite in its bronzy lustre; it is, however, non-magnetic, $D^{25\cdot6} = 4\cdot61$, and analysis II gives the formula FeS, proving the material to be troilite. The stone has $D^{22\cdot6} = 3\cdot48$, and contains: silicates, 87·48; metal, 4·85; troilite, 7·56; schreibersite, 0·11%. Analysis by J. E. Whitfield of the metallic portion gave I, the sulphide II, and of the silicate portion the results under III.

	Fe.	Ni.	Co.	Cu.	S.	Total.
I.	90·50	8·68	0·64	0·29	—	100·11
II.	63·62		nil.		36·50	100·12

	SiO₂.	Al₂O₃.	FeO.	CaO.	MgO.	MnO.	NiO.	Na₂O.	Total.
III.	41·93	4·30	21·85	2·40	29·11	0·25	0·08	trace	99·92

L. J. S.

Meteoric Stones of El Nakhla El Baharia (Egypt). GEORGE T. PRIOR (*Min. Mag.*, 1912, 16, 274—281. Compare A., 1911, ii, 1106; 1912, ii, 361).—One of the stones, weighing 274 grams, of this recent fall was examined. Thin sections show a holocrystalline aggregate of green diopside and brown olivine (there being no hypersthene as stated in previous accounts), with a little interstitial matter consisting of felspar laths. The diopside shows "herring-bone" structure, and its optical constants are $\alpha = 1\cdot685$, $\beta = 1\cdot69$, $\gamma = 1\cdot72$, $2V = 44—48°$, $c:\mathfrak{c} = 40—44°$; its composition II (calculated from I and III) corresponds with $3MgSiO_3,3CaSiO_3,2FeSiO_3$. The olivine is characterised by the presence of dark brown to black enclosures with a definite crystallographic orientation; $\alpha = 1\cdot75$, $\beta = 1\cdot785$, $\gamma = 1\cdot80$, $2V = 67°$; analysis III is of selected grains, and IV of the portion of the stone soluble in hydrochloric acid, corresponding with $2Fe_2SiO_4,Mg_2SiO_4$. This olivine is near to hortonolite, and is much more ferriferous than any meteoric olivine previously described. The bulk analysis of the meteorite is given under I, corresponding with the following mineral composition: diopside, 76·70; olivine, 13·25; felspar, 6·76; magnetite, 1·87; ilmenite, 0·73; chromite, 0·49; troilite (?), 0·17; water, 0·24%.

	SiO₂.	Al₂O₃.	Fe₂O₃.	FeO.	CaO.	MgO.	Total.	Sp. gr.
I.*	48·96	1·74	1·29	19·63	15·17	12·01	100·45	3·47
II.	52·73	—	—	14·93	19·22	13·12	100·00	3·42
III.	32·59	—	—	51·80	1·11	15·60	101·10	3·98
IV.	33·06	—	—	51·67	1·86	13·03	99·62	—

* Also: TiO₂, 0·38; Cr₂O₃, 0·33; MnO, 0·09; Na₂O, 0·41; K₂O, 0·14; S, 0·06, H₂O, 0·24.

Consisting mainly of monoclinic pyroxene and olivine with no metallic iron, this meteorite approaches most closely to the angrite group.
L. J. S.

Meteorite Fall in Central Japan. TETSUGORŌ WAKIMIZU (*Beitr. Min. Japan*, 1912, No. 4, 145—150).—A fall of stones was observed on July 24, 1909, near the town of Gifu, prov. Mino. Twenty-four stones, the largest weighing 4039 grams, were picked up over an area of 12×5 km. The material, D 3·57, is classed as a white chondrite with very little nickel-iron and iron sulphide. Under the microscope it is seen to be holocrystalline, and to consist essentially of olivine and bronzite. Analysis gave :

SiO_2.	P_2O_5.	TiO_2.	Fe_2O_3.	Fe.	Ni.	Mn.	CaO.	MgO.	S.	SO_3.	C.	H_2O.	Total.
41·012	0·458	0·416	5·470	20·583	0·183	0·010	2·768	21·707	2·185	0·201	trace	0·334	99·227

L. J. S.

Analytical Chemistry.

The Estimation of Water and of Carbon Dioxide in Minerals and Rocks. MAX DITTRICH and W. EITEL (*Zeitsch. anorg. Chem.*, 1912, 77, 365—376. Compare A., 1912, ii, 804).—It has not been found practicable to estimate water and carbon dioxide in minerals and rocks by fusion with sodium metaphosphate or borax, as a constant weight is not obtained in blank experiments. On the other hand, heating the material in a stream of dry air in a silica tube is found to be satisfactory. The air supply tube is also of silica, and is ground in and held by springs. A spiral of silver gauze is used to retain sulphur. In the case of minerals which lose water with difficulty, the final heating is performed by means of the blow-pipe. Rocks containing epidote, mica or hornblende often do not lose the whole of their water through these minerals becoming enclosed. Much better results are obtained by the use of a platinum electric furnace surrounding the silica tube. The water is then driven off completely, except in the case of materials containing much fluorine. Calcite does not lose its carbon dioxide completely, unless first mixed with powdered quartz, with a blowpipe, but is completely decomposed in the electric furnace at 1100°. The silica tubes last well at 1000°, but devitrify at higher temperatures. By the use of a platinum-iridium tube and a boat of the same material, the most refractory rocks lose their water and carbon dioxide completely at 1250—1300°.
C. H. D.

New Reagent for Chlorine and Bromine, Free and Combined. GEORGES DENIGÈS and L. CHELLE (*Compt. rend.*, 1912, 155, 1010—1012. Compare A., 1912, ii, 1208 ; Guareschi, *ibid.*, 989).—The reagent is prepared by the addition of 10 c.c. of a solution of magenta

(1 in 1000) to 100 c.c. of sulphuric acid (5% by volume). This is then mixed with an equal volume of acetic acid, and 4 c.c. of strong sulphuric acid are added. This solution is coloured yellow by chlorine and reddish-violet by bromine, the colour being best shown by shaking with chloroform. If the halogens are combined as metallic salts, the solution is acidified, the iodine removed by a ferric salt, the bromine liberated by the addition of potassium chromate and tested for, and the chlorine then liberated by potassium permanganate and separately tested for. The vapours are absorbed in dilute alkali before applying the test. The method can be applied quantitatively for dealing with small quantities of bromine as in natural waters, and is more delicate than the methods at present in use.　　　　　　　　　W. G.

The Iodic Acid Process for the Estimation of Bromine in Halogen Salts. FRANK A. GOOCH and P. L. BLUMENTHAL (*Amer. J. Sci.*, 1912, [iv], 469—474).—A criticism of Bugarszky's process (boiling the solution containing bromides and chlorides with potassium iodate and dilute sulphuric acid and determining the loss in iodine: A., 1896, ii, 216).

The authors find that although the process was thought to be an ideal one, it is vitiated by secondary effects. The latter may be reasonably attributed to the action of small amounts of iodine monochloride or monobromide formed in the interaction of iodic acid and free iodine with hydrochloric acid and hydrobromic acid.

Substitution of chloric acid for iodic acid cannot be recommended.
　　　　　　　　　　　　　　　　　　　　　　　　　L. DE K.

Oxidisable Substances in the Air. L. SCHWARZ and GEORG MÜNCHMEYER (*Chem. Zentr.*, 1912, ii, 1695; from *Zeitsch. Hyg. Infekt.-Krankh.*, 1912, 72, 371—384).—Henriet and Bouyssy's method (A., 1911, ii, 532) whereby the titration of condensed water is taken as a measure of the degree of vitiation of an atmosphere, is criticised. Such condensed water gives different readings at different temperatures, and would only give a correct value if all the moisture in the atmosphere could be condensed, or if it contained oxidisable substances to the same extent as the collected water, which is not the case.　　　　　　　　　　　　　　　　　　J. C. W.

An Apparatus for Microanalysis of Blood Gases and Micro-respirometry. HANS WINTERSTEIN (*Biochem. Zeitsch.*, 1912, 46, 440—449).—The apparatus (which is figured) is a combination of the Barcroft-Haldane and Petterson systems. It consists essentially of two pear-shaped flasks, one of which is a compensation flask, and the other serves for the actual analysis. They communicate by means of three-way stopcocks either with the outer air or with one another. The latter communication is through an otched capillary tube containing an oil drop. The analysis flask communicates, furthermore, with a manometer, of which the narrower limb which is nearer the flask is a capillary, graduated in millimetres. The outer limb is broader, and is closed by a piece of indiarubber with a screw-clamp, and a piece of solid glass rod. The flasks communicate; the meniscus of the oil drop in the capillary connecting the two

flasks is brought to a certain point by turning the screw-clamp on the indiarubber, and the height of the mercury in the graduated limb of the manometer is then read. This takes place with the same materials in each flask, and the whole apparatus is kept in a water-bath. If the measurement to be carried out consists in the determination of the oxygen content, Haldane's ferricyanide method is employed, the reagent being kept in spoons fused on to the stoppers. The apparatus, after the first reading and adjustment, is then removed from the water-bath and shaken, so as to bring the ferricyanide into the blood and ammonia mixtures, whilst the two flasks are kept closed and out of communication with one another. They are then brought back to the water-bath, brought into communication, the position of the oil drop in the communicating flask is readjusted, and the height of the manometer is read. The difference between this and the original reading gives the amount of oxygen evolved.

S. B. S.

Estimation of Tellurium by means of Hydrazine Hydrate. J. B. Menke (*Zeitsch. anorg. Chem.*, 1912, 77, 282—288).—See this vol., ii, 41.

Detection of Nitrogen in Organic Substances. H. Zellner (*Pharm. Zeit.*, 1912, 57, 979—980).—For the detection of small quantities of nitrogen, or when the amount of the substance to be tested is not large, the following modification of the usual test may be employed. The substance is fused with potassium, the fused mass is dissolved in water, and the solution is warmed after the addition of ferrous sulphate. The solution is then filtered, and the filtrate is poured on the surface of ferric chloride solution acidified with hydrochloric acid. If nitrogen is present in the substance, a blue zone appears at the junction of the two liquids.   W. P. S.

A New Gas-analytical Method for the Estimation of Nitric Oxide. I. Oskar Baudisch and Gabriel Klinger (*Ber.*, 1912, 45, 3231—3236).—The method depends on the fact that when air is passed into nitric oxide standing in contact with solid potassium hydroxide, nitrogen trioxide (N_2O_3) is formed, and immediately converted by the hydroxide into potassium nitrite, there being no formation of nitrogen dioxide. Four-fifths of the contraction thereby caused is due to nitric oxide, as expressed by the equation : $4NO + O_2 + 4KOH = 4KNO_2 + 2H_2O$.

The analysis is carried out in Fuller's gas-analysis apparatus ; the pipette contains slightly moistened stick potassium hydroxide, with which the nitric oxide is in contact before air is passed in, and all measurements are carried over mercury. Before passing the nitric oxide into the pipette the latter is completely filled with mercury.

The method gives accurate results, even in the presence of nitrous oxide or hydrogen. The reverse method of passing the nitric oxide into air standing over potassium hydroxide cannot be used, since a mixture of N_2O_3 and NO_2 ie formed.   T. S. P.

Detection of Nitrous Acid in Water. PRIMOT (*Chem. Zentr.*, 1912, ii, 1846—1847; from *Bull. Sci. Pharmacol.*, 1912, 19, 546—547). —To 10 c.c. of the water 4 or 5 drops of a 1—1·5% solution of benzidine, *o*-tolidine, or dianisidine in 30—40% alcohol are added. The mixture is then acidified with 5 or 6 drops of acetic acid and shaken, when the development of a yellow colour, which deepens in time, shows the presence of a nitrite. Benzidine is the least sensitive reagent. The limit of sensitiveness is below 0·01 mg. of nitrous acid per litre. J. C. W.

Estimation of Nitrates with Indigo. LUIGI ERMANNO CAVAZZA (*Chem. Zentr.*, 1912, 11, 1061—1062; from *Atti II. Congr. Naz. Chim. applic.*, 1912).—Ten grams of powdered pure indigo are introduced (with cooling) in small quantities into 50 c.c. of fuming sulphuric acid, and after forty-eight hours the solution is diluted to a litre. Fifty c.c. of the liquid are then diluted so that 10 c.c. correspond with 0·001 gram of nitrogen pentoxide. When dealing with nitrates, a stronger solution may he employed. Organic matters if present should be removed by adding to 25 c.c. of the solution the requisite amount of potassium permanganate (previously determined); 30 c.c. of sulphuric acid are added, and the whole heated over a small flame and titrated. When the liquid turns bright yellow, the heating is discontinued and the titration rapidly brought to an end. In testing ordinary water, concentration by evaporation is not necessary as the end reaction is so very sensitive. L. DE K.

The Marsh Arsenic Test. GEORG LOCKEMANN (*Chem. Zeit.*, 1912, 36, 1465—1466).—Historical. The original Marsh apparatus and modifications of it are described. L. DE K.

Estimation of Small Quantities of Carbon Monoxide. OTTO BRUNCK (*Zeitsch. angew. Chem.*, 1912, 25, 2479—2481).—A suitable flask of known capacity (say, a litre flask) is fitted with a doubly perforated rubber cork closed by means of rods. After filling the flask with the air to he examined, 50 c.c. of sodium palladium chloride (1 c.c. = 0·004762 gram of palladium) are introduced from a pipette (while gently loosening the second rod), followed by 25 c.c. of 5% solution of sodium acetate; the volume of liquid is, of course, deducted from the volume of the gas tested.

After an hour's action with frequent shaking, the palladium which has deposited owing to the reducing action of the carhon monoxide is collected and ignited with the usual precautions; 1 gram of metallic palladium = 0·2624 gram, or 210 c.c. of carbon monoxide.

Hydrogen and the unsaturated hydrocarbons should he absent, as they also exert a reducing action. L. DE K.

Simple Apparatus for the Estimation of Carbon Dioxide. W. R. FORNES (*Chem. News*, 1912, 106, 284).—The apparatus consists essentially of an inverted V-tube closed at either end and provided in the middle with a ground stopper carrying a delivery tube and tap. In use, the acid is placed in one limh and the carbonate in the other. Reaction is started by suitably inclining the apparatus. H. W.

Cobaltinitrite Method of Estimating Potassium. F. H. MacDougall (*J. Amer. Chem. Soc.*, 1912, 34, 1684—1686).—In the estimation of potassium by the cobaltinitrite method, it is usual to boil the yellow precipitate with excess of $N/10$-potassium permanganate, then add dilute sulphuric and oxalic acids, and finally to titrate with $N/10$-permanganate. The oxidation of the nitrite thus takes place in alkaline solution, and the permanganate is reduced to manganese dioxide. The latter reacts but slowly with the oxalic acid added subsequently, since the mixture is so dilute. The author has therefore studied the effect of adding dilute sulphuric acid to the yellow precipitate before oxidising it with permanganate.

It has been found that accurate results can be obtained in this way, but that a different factor must be employed in the calculation ; according to the usual method, 1 c.c. of $N/10$-permanganate is equivalent to $0\cdot0007111$ gram K or $0\cdot0008564$ gram K_2O, whilst with the modified method, 1 c.c. of $N/10$-permanganate corresponds with $0\cdot0006518$ gram K or $0\cdot0007850$ gram K_2O.   E. G.

Determination of the Sensitiveness of the Hydroxide Reactions for the Common Metals. Louis J. Curtman and A. D. St. John (*J. Amer. Chem. Soc.*, 1912, 34, 1679—1684).—A study has been made of the sensitiveness of the hydroxide test for metals. The experiments consisted in treating a solution of a salt of the metal with 10% ammonia or sodium hydroxide, the final volume being 5 c.c. In the following cases, ammonia was used as the precipitant and the limiting concentrations of the metals at which a precipitate was visible were : lead, 1—6500; mercury (in the mercuric state), 1—13,000; bismuth, 1—10,000 ; iron, 1—80,000 ; aluminium, 1—100,000 ; chromium, 1—170,000; zinc, 1—80,000. For the following metals, sodium hydroxide was employed as the reagent and the limits found were : silver, 1—40,000 ; mercury (in the mercurous state), 1—200,000; copper, 1—10,000 ; cadmium, 1—40,000 ; nickel, 1—80,000 ; cobalt, 1—80,000 ; magnesium, 1—10,000. In the case of manganese, either ammonia or sodium hydroxide can be used, the limiting concentration in each case being 1—170,000.   E. G.

Estimation of Lead in Lead Paints. Franz Utz (*Chem. Zentr.*, 1912, ii, 1788 ; from *Farbenzeit.*, 18, 18—20).—The nitric acid solution of the lead compound is electrolysed at 60—65° by a current of $0\cdot05$—$1\cdot5$ amperes, using gauze electrodes, and the lead dioxide is washed without breaking the current and then dried at 200°.   J. C. W.

Cuprous Iodide. Moritz Kohn and Arthur Klein (*Zeitsch. anorg. Chem.*, 1912, 77, 252—254).—Cuprous iodide may be analysed by the method of Bauhigny and Chavanne for iodine in organic substances (A., 1903, ii, 510 ; 1904, ii, 203). One to $1\cdot5$ gram of silver nitrate is dissolved in 40 c.c. of concentrated sulphuric acid in a flask, and, after cooling, 5 grams of pure potassium dichromate are added. This is then dissolved by warming, and the whole is again cooled. After adding $0\cdot3$ gram of the substance, the flask is warmed

and shaken until the evolution of oxygen begins. The silver iodide formed at first dissolves as iodate. After cooling, the contents of the flask are poured into 80 c.c. of water, reduced by sodium sulphite, and allowed to remain until the silver iodide has settled. This is collected on a Gooch filter after the addition of nitric acid, dried at 130°, and weighed.

Copper is estimated by heating 0·5 gram of the substance with 15—20 c.c. of nitric acid (1:1), converting into sulphate, and precipitating as sulphide.

Like potassium bromide (Kohn, A., 1909, ii, 891), ammonium bromide solutions dissolve cuprous iodide, the solubility increasing rapidly with the concentration.   C. H. D.

Sensitiveness of the Bead and Lead Dioxide Tests for Manganese with Special Reference to the Interference of Iron. Louis J. Curtman and A. D. St. John (*J. Amer. Chem. Soc.*, 1912, **34**, 1675—1679).—A study has been made of the sensitiveness of the bead and lead dioxide tests for manganese and the influence of iron on those tests. The results show that the lead dioxide test is not trustworthy in presence of 300 or 400 parts of iron to 1 part of manganese unless as much as 0·2 mg. of manganese is present, but that the bead test is efficient with larger quantities of iron provided that as much as 0·005 mg. of manganese is introduced into the bead and certain specified precautions are observed.   E. G.

Estimation of Iron in Water. F. König (*Chem. Zentr.*, 1912, ii, 1064; from *Apoth. Zeit.*, **27**, 536—537).—Klut's nitric acid process (*ibid*, 1909, ii, 1076) for the colorimetric estimation of iron in waters gives good results with samples absorbing not more than 80 mg. of potassium permanganate per litre. When this amount is exceeded, the iron should be estimated, colorimetrically, in the residue after ignition.   L. de K.

Reagent for Detecting Small Quantities of Nickel. V. Fortini (*Chem. Zeit*, 1912, **36**, 1461).—The following solution is recommended for the detection of nickel in plated wares and nickel alloys. 0·5 Gram of dimethylglyoxime is dissolved in 5 c.c. of 98% alcohol, and 5 c.c. of ammonia are added. After rinsing the surface with ether, a drop of the reagent is applied, when a rose-coloured spot will form should nickel be present. Previous heating in the oxidation flame will render the test still more delicate. The presence of other metals usually present does not interfere. The spot formed may be easily removed with a towel.   L. de K.

Test for Methane. I. Otto Hauser and H. Herzfeld (*Ber.*, 1912, **45**, 3515—3516).—Methane and ozonised oxygen react with each other with the formation of formaldehyde, which reaction may be used as a very delicate test for methane. The gas to be tested is mixed with ozonised oxygen and the mixture passed through a tube containing moistened glass wool, which is afterwards extracted with water and the solution tested for formaldehyde with morphine and sulphuric acid.

Methane is the only hydrocarbon which gives formaldehyde. Ethane gives acetaldehyde or acetic acid, but the reaction is much slower than with methane, whilst acetylene is oxidised explosively to carbon dioxide. The reaction with acetylene takes place also in acetone solution, and is accompanied by a beautiful green luminescence. Toluene is oxidised by ozone with formation of formic acid.

<div align="right">T. S. P.</div>

Analysis of Hydrocarbon Mixtures. OSCAR ROUTALA (*Chem. Zentr.*, 1912, ii, 638; from *Ann. Acad. Sci. Fennicae, A.*, 2, No. 13, 19 pp.).—The iodine absorption process for the testing of petroleums is too much affected by the personal equation, and reports founded on it should be accompanied by a careful description of details of analysis, including time of action, temperature, exposure to light, and volume of iodine solution added. Frank's bromine process (*Chem. Ind.*, 1901, 24, 263) may be successfully applied when small quantities of the substance are to be tested, also when the refining degree of colourless or pale petroleum products has to be determined, or when the degree of purity of olefines has to be ascertained. From the bromine number the percentage of the olefine is calculated directly by the formula $A = [K + (n-5)c].G$, in which A = % of the olefine, K = a constant, n the mean number of carbon atoms for the olefine boiling at between the limits of temperature (at least 5), c = a constant ($= 0.875°$), and G the bromine number. For amylene, $K = 0.4375$; for hexylene, 0.5950; for heptylene, 0.6075; for each additional CH_2-group, the constant increases on the average by 0.0875. To show the accuracy of the formula a bromine number was taken of a mixture of amylene and *iso*pentane, and the result agreed with the sulphuric acid process and the density.

<div align="right">L. DE K.</div>

Methoxyl Estimation with Hydriodic Acid and Phenol. FRITZ WEISHUT (*Monatsh.*, 1912, 33, 1165—1172).—It is found that many substances which fail to give satisfactory results for the estimation of the methoxyl group, even in the presence of acetic anhydride, can be made to do so by using a mixture of hydriodic acid with approximately one-quarter its volume of phenol. In most cases the reduction is complete in about one and a-half hours, but methyl nitroanisate required five and a-half hours.

<div align="right">D. F. T.</div>

Estimation of Higher Alcohols in Wine. THEODORE VON FELLENBERG (*Chem. Zentr.*, 1912, ii, 1851; from *Mitt. Lebensmitt. Hyg.*, 3, 231—235).—The colour reaction which higher alcohols give with salicylaldehyde and concentrated sulphuric acid (A., 1911, ii, 667) has been applied to wine. Natural wines are found to contain about three parts per 1000 of higher alcohols, which suggests that the accepted value for cognac (1 per 1000) is very low.

<div align="right">J. C. W.</div>

A Colour Reaction of Wine. THEODORE VON FELLENBERG (*Chem. Zentr.*, 1912, ii, 1850—1851; from *Mitt. Lebensmitt. Hyg.*, 3, 228—231).—A colour reaction which phloroglucinol gives with vanillin and hydrochloric acid is also obtained with wine, which

prohably contains, therefore, an unsaturated alcohol. The red colour may he matched against a standard solution of acid magenta.

<div align="right">J. C. W.</div>

Examination of Lead Precipitates in Wine; Pentose and Methylpentose Estimations in Grapes and Wine. THEODORE VON FELLENBERG (*Chem. Zentr.*, 1912, ii, 1850; from *Mitt. Lebensmitt. Hyg.*, 3, 213—217).—After precipitation with just the required amount of lead acetate (found hy a series of preliminary tests) there are still some suhstances in natural wines, although scarcely at all in sophisticated wines, which may he precipitated hy hasic lead nitrate. The precipitate contains succinic acid, inositol, pectin, pentosan, and methylpentosan. The pectin of grapes contains pentose and methylpentose, but does not account for the whole of these sugars, which are present both in the free state, unprecipitable by basic lead nitrate, as well as in the form of pentosans.

<div align="right">J. C. W.</div>

A Simple Method of Characterising Acraldehyde. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1912, 524).—The acraldehyde vapour is condensed in distilled water, through which a slow stream of oxygen is then passed until the solution is strongly acid. On dissolving freshly precipitated silver oxide in this liquid and concentrating the clear solution, silver acrylate crystallises out in the pure state.

<div align="right">W. G.</div>

A Bromometric Estimation of Formic Acid. H. MÄDER (*Chem. Zentr.*, 1912, ii, 1401; from *Apoth. Zeit.*, 1912, 27, 746—747). —A method for the estimation of formic acid is given; it depends on the oxidation of the acid hy bromine. The solution is left for twelve to fifteen hours with hromide and bromate of potassium and phosphoric acid in a stoppered bottle, when the unused bromate is decomposed hy potassium iodide and estimated with thiosulphate.

<div align="right">J. C. W.</div>

The Detection of Acetoacetic Acid by Sodium Nitroprusside and Ammonia. VICTOR JOHN HARDING and ROBERT FULFORD RUTTAN (*Bio-Chem. J.*, 1912, 6, 445—450).—Le Nobel's test for acetone in the urine, in which the urine is treated with acetic acid, sodium nitroprusside and ammonia, was found to give a less distinct reaction with urine to which acetone had been added than in natural acetonuric urines; furthermore, in the lattor cases the reaction was less distinct in distillates containing relatively large amounts of acetone than in the original urine. The authors ehow now, that the Le Nohel test is really a reaction for acetoacetic acid and not for acetone, and as such it is capable of detecting 1 part of this acid in 30,000, whereas the ordinary ferric chloride test fails when the dilution is only 1 in 7000.

<div align="right">S. B. S.</div>

Detection of Benzoic Compounds. OTTO SCHMATOLLA (*Pharm. Zeit.*, 1912, 57, 947).—Twenty c.c. of a solution to be tested for the presence of benzoic acid are mixed with 5 c.c. of hydrogen peroxide

and a solution, prepared by dissolving 5 grams each of ferrous sulphate and boric acid in 100 c.c. of water, is added until the mixture no longer becomes darker in colour. Should benzoic acid be present, a dark bluish-green coloration develops with a few seconds. The test will detect the presence of 1 part of benzoic acid in 15,000 parts of solution. A similar reaction is given by all benzoic compounds, hippuric acid, etc. Benzoic acid, however, may be separated from hippuric acid in mixtures of the same by extracting the former acid with light petroleum. By means of suitable solvents, benzoic acid may be separated from salicylic acid, and then identified by the above reaction.   W. P. S.

Nature of the Reactions of Naphthenic Acids. K. W. CHARITSCHKOV (*Chem. Zeit.*, 1912, **36**, 1378. Compare A., 1910, ii, 549 ; 1911, ii, 543).—The reactions of naphthenic acid described previously with copper sulphate, ferrous salts, cobalt nitrate, and hydrogen peroxide are characteristic of *cyclo*pentanemonocarboxylic acids, and are not shown by acids which contain the *cyclo*hexane ring, such as *cyclo*hexylacetic acid.   H. W.

A New Method for the Colorimetric Estimation of Uric Acid in Urine. OTTO FOLIN and A. B. MACALLUM, jun. (*J. Biol. Chem.*, 1912, **13**, 363—370).—The method is based on the colour produced by the action of phosphotungstic acid.   W. D. H.

Detection and Estimation of Arachis Oil. NORMAN EVERS (*Analyst*, 1912, **37**, 487—492).—After trying various methods already proposed, the author gives the following process : 5 grams of the sample (say, olive oil) are saponified with 25 c.c. of alcoholic potassium hydroxide (80 grams in 80 c.c. of water and diluted to a litre with 90% alcohol) in a reflux apparatus. To the hot soap solution are added 7·5 c.c. of dilute glacial acetic acid (1:2) and 100 c.c. of 70% alcohol containing 1 vol.% of hydrochloric acid, and the liquid is then cooled to 12—14° for an hour. The deposit is collected and washed with the acid alcohol (temp. 17—19°) until the filtrate gives no turbidity with water, the washings being measured. The precipitate, according to its bulk, is dissolved in 25 to 70 c.c. of hot 90% alcohol and cooled to 15—20°. If abundant crystals appear, then after one to three hours they are collected and washed, first with 90% alcohol (about half the volume used for crystallisation), and finally with 50 c.c. of 70% alcohol. The crystals are now dissolved in hot ether, and this is then distilled off in a weighed flask ; the residue is dried at 100° and weighed. Should the m. p. be lower than 71°, the acid should be recrystallised from 80% alcohol. A correction for solubility should be made, for which a table is given. If no, or but few, crystals are obtained from the 90% alcohol, a sufficient quantity of water is added to reduce this to 70% strength. Any deposit then formed within an hour at 17—19° is collected, washed with 70% alcohol, and weighed as before, applying the correction for solubility. It must be recrystallised if the m. p. is below 71°.

4·54 Grams of crystals = 100 grams of arachis oil. The following

oils gave no crystals : olive oils, including three superfine Maloga and eight of unknown origin, almond, poppy, and rape oils.   L. DE K.

Estimation of Cyanogen Compounds in Gas-Liquors. FRANZ WEISSER (*Chem. Zeit.*, 1912, **36**, 1285—1287).—*Estimation of ammonium cyanide.*—This is found by difference from the total cyanogen and that present as ferrocyanide. *Total cyanogen.*—500 c.c. of the liquor are mixed with 50 c.c. aqueous potassium hydroxide (1 : 1) and 50 c.c. 10% ferrous sulphate, and heated for one to two hours on the water-bath.   After cooling and diluting to a litre, 100 c.c. of the filtrate are acidified with hydrochloric acid, and 5 c.c. of 10% ferric chloride are added.   The Prussian-blue formed is collected and then again decomposed with dilute aqueous potassium hydroxide.   The filtrate, which contains all the cyanogen as ferrocyanide, is evaporated with excess of sulphuric acid, and the residue is gently ignited.   The residual iron oxide is then estimated as usual by titration with permanganate.   One c.c. of $N/100$-permanganate $= 0.00156$ gram of cyanogen.

Ammonium ferrocyanide.—100—500 c.c. of the liquor are evaporated, and the residue is gently ignited.   The iron is then titrated as usual ; 1 c.c. of $N/100$ permanganate $= 0.00284$ gram of the ferrocyanide.

Ammonium thiocyanate.—The author has slightly modified Pfeiffer's colorimetric process.   Fifty c.c. of the sample are diluted with 50 c.c. of water, and evaporated on the water-bath to 30 c.c. so as to expel the free ammonia.   After diluting to 100 c.c., 20 c.c. of the solution (= 10 c.c. of sample) are mixed with 10 c.c. of ferric chloride solution (5 parts of the salt made up to 100 parts with 10% hydrochloric acid) and diluted to 500 c.c.   An aliquot part of the liquid is then matched as usual with a solution of ammonium thiocyanate of known strength.   L. DE K.

Estimation of Scatole and Indole in Fæces. CURT MOERWES (*Chem. Zentr.*, 1912, ii, 1702 ; from *Zeitsch. expt. Path. Ther.*, 11, 555). —The scatole and indole obtained by extracting the steam distillate with light petroleum are precipitated by dimethylaminobenzaldehyde, and the dye is dissolved in water and compared in a Plesch chromophotometer with a test solution of 1 : 100,000 made from equal parts of iodole and scatole.   Values of 0·008—0·024 gram per 100 grams of fæcal matter were obtained.   · J. C. W.

Action of Activated Aluminium on Alkaloidal Extracts: Its Use in Toxicology. EMILE KOHN-ABREST (*Compt. rend.*, 1912, 155, 1179—1181.   Compare A., 1912, ii, 648—768).—A study of the behaviour of the more common vegetable alkaloids, pure, or mixed with viscera, in the presence of activated aluminium.   The hydrated oxide formed from the activated aluminium only fixes a certain small proportion of alkaloids, such as strychnine, quinine, and cocaine in alcoholic solution acidified with tartaric acid, whilst on the other hand it retains almost all the nicotine.   Data are given for some fourteen alkaloids.   Alcoholic extracts of viscera containing morphine

and strychnine, after treatment with activated aluminium, are obtained in a state of great purity, wherein the alkaloids can be readily detected and estimated.   W. G.

Distinction between Cocaine and its Substitutes. D. SCHERBATSCHEV (*Chem. Zentr.*, 1912, [ii], 386; from *Apoth. Zeit.*, 1912, 27, 441. Compare Hankin, A., 1911, ii, 162).—The appearance under the microscope of solutions of β-eucaine, nirvanine, alypine, holocaine, and novocaine, when solutions of ammonia (10%), potassium hydroxide (10%), or sodium hydrogen carbonate (saturated) are added to them, is described.   T. A. H.

Gravimetric Estimation of Quinine as Nitroprusside. P. J. KRUYSSE (*Pharm. Weekblad*, 1912, 49, 1117—1120).—Quinine nitroprusside is obtained as a crystalline precipitate when a neutral solution of a quinine salt is treated with sodium nitroprusside; its solubility is less than that of the tartrate or oxalate, 100,000 parts of water dissolving 39 parts of the salt. For the estimation of quinine in powdered cinchona bark, 5 grams of the latter are mixed with 3·5 c.c. of water, 1 c.c. of ammonia and 2·5 grams of slaked lime, and the mixture is extracted in a Soxhlet apparatus for two hours with acetone. After the acetone has been evaporated from the extract, the residue is dissolved in 25 c.c. of 2% hydrochloric acid, the solution is filtered, rendered alkaline, and shaken with ether. The ethereal solution is then shaken with dilute hydrochloric acid, the separated acid solution is neutralised, diluted to 50 c.c., heated to 90°, and treated with 0·5 gram of ammonium oxalate. After cooling, the precipitate is collected on a filter, washed with a small quantity of water, and then dissolved in 5 c.c. of 2% hydrochloric acid. This solution is nearly neutralised, and the excess of oxalate is removed as calcium oxalate. The solution is now neutralised with ammonia, diluted to 70 c.c., heated to boiling, and treated with 0·5 gram of sodium nitroprusside. After cooling, the precipitate is collected, washed with water, dried at 100°, and weighed. The treatment with ammonium oxalate is for the purpose of separating cinchonine from the quinine.
                                                        W. P. S.

Estimation of Quinine Sulphate in Cinchona Bark. P. J. KRUYSSE (*Pharm. Weekblad*, 1912, 49, 1135—1136).—The author (preceding abstract) regrets he was not acquainted with the work of Kramers (A., 1897, ii, 83), who, however, did not succeed in applying the nitroprusside reaction quantitatively.   L. DE K.

Hyposulphite in Volumetric Analysis. I. WILHELM SIEGMUND (*Monatsh.*, 1912, 33, 1431—1445).—The hyposulphites give stable compounds with the ketones, which, in contradistinction to the form-aldehyde-hyposulphites, act as reducing agents in the cold. Solutions of these compounds may therefore be used as standard reducing agents in volumetric analysis. The author finds that a convenient solution has the following composition: 10 grams of sodium hyposulphite, 15 c.c. of acetone, and 35 c.c. of ammonia (D = 0·91) to one litre of

water. The solution is kept, under a layer of paraffin oil, in a stock bottle from which a burette can be filled automatically; the top of the liquid in the burette is covered with toluene to prevent contact with the air. The tip of the burette is connected with the titration flask by means of a piece of glass tubing, which is bent twice at right angles, and passes through the rubber stopper of the flask. The stopper also contains inlet and exit tubes for a current of oxygen-free carbon dioxide, and a thermometer.

The solution of the hyposulphite is standardised by means of iron alum, or an oxidised solution of ferrous ammonium sulphate, using ammonium thiocyanate as indicator, and in the presence of sulphuric acid. The titration is carried out in the cold, with vigorous shaking; the sulphite formed has no action on the ferric salt. The solution is fairly stable, but should be standardised daily.

Experiments with a large number of azo-dyes, dyes which form leuco-compounds and nitro-colouring matters, show that they are reduced quantitatively by the above hyposulphite solution.

T. S. P.

Methods of Estimating Saponins. (Mlle.) MARIE KOBSAKOV (*Compt. rend.*, 1912, **155**, 844—846).—A critical study of the methods at present employed for estimating saponins. Christophson's method based on the precipitation of the saponin as a barium compound is inaccurate, since the whole of the saponin does not separate, and further the barium hydroxide precipitates, from plant extracts, other substances than saponins, which on hydrolysis yield dextrose. A modification of Kruskul's method gives good results. The plant is dried, finely powdered, and extracted with boiling alcohol (60%). The extract is filtered, the alcohol distilled off, and the residue evaporated on the water-bath with calcined magnesia. The resulting paste is extracted with boiling alcohol (80%), the extract filtered, and precipitated with ether. The precipitate is dissolved in 3% sulphuric acid, and hydrolysed in an autoclave at 105° for one hour, the sapogenin liberated being washed with water, dissolved in absolute alcohol, and weighed after distilling off the alcohol. W. G.

A Delicate Test for the Detection of Albumin in Urine. ADOLF JOLLES (*Zeitsch. physiol. Chem.*, 1912, **81**, 205—206. Compare A., 1896, ii, 344).—The reagent is composed of mercuric chloride, 10 parts, citric acid 20 parts, sodium chlorate 20 parts, water 500 parts. Five c.c. of the filtered urine are added to each of three test-tubes. To (1) and (2) 1 c.c. of 30% acetic acid is added, 5 c.c. of the reagent are put in (1), and the other tubes are filled with water to the same level. The tubes are observed against a black background, (3) being placed in the middle. The reaction is sensitive to 1 part of albumin in 120,000. E. F. A.

Chemistry and Estimation of Gelatin. M. BERRÀR (*Biochem. Zeitsch.*, 1912, **47**, 189—214).—Gelatin forms saturated solutions in water in the following strengths: 0·62% at 21°, 0·60% at 18°, and 0·56% at 17°. If the concentrations only slightly exceed these pro-

portions, a gel is formed. Gelatin cannot be precipitated quantitatively by alcohol, or by metaphosphoric acid, as it completely dissolves in excess of the latter reagent, the proteins being only partly soluble in excess. At room temperature it is not precipitated quantitatively by picric acid, but at 8° precipitation is complete when a gelatin solution is mixed with a saturated aqueous solution of the acid. The acid combining power of gelatin was estimated by precipitation with potassium-mercuric iodide and picric acid solutions. Hydrochloric acid could not be used for this purpose, as the precipitate dissolves in excess of the acid. By this means it was found that 1 gram of gelatin combines with the equivalent of 11·3 c.c. $N/10$-acid, which corresponds with a molecular weight of 823. The picric acid precipitate of gelatin dissolves in alcohol and in 2% urea solution containing sodium chloride. If a mixture of 1 part of saturated aqueous solution of picric acid and 4 parts of alcohol are added to a gelatin solution, the gelatin is not precipitated, whereas other proteins are. The gelatin is, however, precipitated quantitatively from this gelatin-picric acid solution in alcohol by the addition of excess of aqueous picric acid solution in the cold. The precipitate again dissolves on warming to 40°, or treating again with absolute alcohol. On these reactions a method is based for estimating quantitatively gelatin in the presence of other proteins. It was incidentally observed that the nitrogen in picric acid can be quantitatively estimated by Kjeldahl's process, if it is first reduced by iron and glacial acetic acid.   S. B. S.

The Rideal-Walker Phenol Control. A Possible Discordant Factor in the Standardisation of Disinfectants. J. T. AINSLIE WALKER and JOHN M. WEISS (*J. Franklin Inst.*, 1912, 101—112).— The accuracy of the Rideal-Walker process depends on the purity of the phenol which is employed as the standard. Ordinary crystallised phenol is usually contaminated by cresols to such an extent as to render it unsuitable for the purposes of bactericidal control ; four specimens of phenol examined by the authors were found to contain from 1·1 to 12·8% of cresols. As cresol has approximately three times the bactericidal efficiency of phenol, the error from this cause may be very considerable. The purity of the phenol should be ascertained by a determination of its solidifying point, and phenol having a lower solidifying point than 40° should be rejected. Synthetic phenol prepared by the authors showed a solidifying point of 40·5°. The bromine titration method does not yield trustworthy results as regards the purity of the phenol, but it may be employed for checking the strength of the 5% stock solution prepared from pure phenol.   W. P. S.

General and Physical Chemistry.

New Observations Relative to the Zeeman Effect in the Hydrogen Spectrum. F. CROZE (*Compt. rend.*, 1912, 155, 1607—1610. Compare A., 1912, ii, 613).—The author has extended his study of the Zeeman effect in the case of hydrogen to the δ-line, and has made new measurements, for this line and the α-, β-, and γ-lines, of the value of $\Delta\lambda$ in a field of 24,122 gauss. He maintains his previous view that these three rays furnish a pure triplet with normal deviation, and replies to Paschen and Back (*Ann. Physik.*, 1912, [iv], 39, 897), putting forward an explanation as to why their results differ from his.   W. G.

The Dispersion of Certain Metals in the Visible Spectrum. CONSTANTIN ZAKRZEWSKI (*Bull. Acad. Sci. Cracow*, 1912, 842—849).— A formula is deduced, by means of which the optical constants of a metal can be calculated from the phase differences of the components, parallel and perpendicular to the plane of incidence, measured for two different angles of incidence. This method of obtaining the constants does not, like the usual method, involve the preparation of highly polished metallic mirrors. The formula is applied to data obtained by the author for nickel and zinc, and to Drude's measurements for silver.   H. M. D.

Electric Behaviour of Certain Vapours which Exhibit Absorption Bands. F. BURGER and JOHANNES KOENIGSBERGER (*Physikal. Zeitsch.*, 1912, 13, 1198—1199).—The nature of the process which gives rise to banded emission and absorption is further discussed (compare A., 1912, ii, 405). Bromine and nitrogen peroxide exhibit banded spectra, and experiments with these substances are described which show that the carriers responsible for the banded spectra in these two cases cannot be due either to electrons or free ions so far as the visible spectrum is concerned. An upper limiting value for the proportion of ionised molecules is calculated, which also indicates that the banded absorption cannot be attributed to the occurrence of ionised molecules.   H. M. D.

The Absorption Curve of Colloidal Silver Solutions. R. GANS (*Physikal. Zeitsch.*, 1912, 13, 1185—1186).—On the assumption that the colloidal particles have the form of ellipsoids of rotation, the author has calculated the form of the absorption curve for the region $\lambda = 4200$ to $\lambda = 7500$ for varying values of the axial ratios. As in the case of gold solutions (A., 1912, ii, 508) the curve thus obtained may be utilised in the investigation of the geometrical form of the particles present in colloidal solutions of silver.   H. M. D.

The Influence of Acid Radicles on the Colour Intensity of Copper Salts. CHARLES SCOTT GARRETT (*Zeitsch. Elektrochem.*, 1913, 19, 1—7).—The molecular extinction of a number of soluble

copper salts was determined by means of a Hüfner spectrophotometer. The salts $CuCl_2$, $CuBr_2$, $Cu(NO_3)_2$, $Cu(ClO_3)_2$, $CuCr_2O_7$, $CuSO_4$, and $Cu(ClO_4)_2$ were examined at concentrations from $1n—0·01n$. The experimental results are discussed and interpreted on the basis of Baly's theory of the action of a solvent on a dissolved substance. It is shown (1) that when a concentrated solution is diluted, a penetration of the salt molecule system by the solvent molecule system occurs; (2) the mean number of solvent molecules, the fields of force of which penetrate the field of force of the dissolved molecule, conditions the process of solution at a given concentration; (3) every vibration of the copper atom in the undissociated molecule, which is active in the absorption of light, is influenced by the free electric field of the typical atoms of the acid radicle; (4) the light absorption due to the copper is not specifically influenced by the presence of a coloured acid radicle, as is frequently the case with organic substances, and (5) there is a strengthening of the light absorption when the free electric field of the acid radicle is negative.   J. F. S.

Absorption Spectra of Solutions as Affected by Temperature and by Dilution. Quantitative Study of Absorption Spectra by means of the Radiomicrometer. HARRY C. JONES and J. SAM GUY (*Amer. Chem. J.*, 1913, 49, 1—46).—In an earlier paper (A., 1912, ii, 70) an account was given of a study of the effect of heat and of dilution on the absorption spectra of certain neodymium salts. The work on these salts has now been continued and the investigation has been extended to praseodymium nitrate and chloride, and to uranyl nitrate and sulphate. The radiomicrometer employed was a slightly modified form of that described previously.
                                                      E. G.

Quantitative Investigation of the Absorption of Ultra-violet Rays by the Fatty Acids and their Isomeric Esters. JEAN BIELECKI and VICTOR HENRI (*Compt. rend.*, 1912, 155, 1617—1620. Compare A., 1912, ii, 882).—The authors have made a more detailed comparison of the absorptive power in the case of three fatty acids and the esters isomeric with them, and in the case of a number of groups of isomeric esters, the absorption being measured in aqueous and alcoholic solutions and with rays of varying wavelengths. Curves and tables are given, and the results show that (1) the absorption spectrum of the various acids is different from that of the esters isomeric with them, this difference being independent of the solvent; (2) the absorption of the ultraviolet rays is controlled by the molecular complexity and augments with increasing complexity. There is also a considerable variation in the absorption spectra of the isomeric esters, dependent on the molecular arrangement, as is shown by a study of the four esters, butyl acetate, propyl propionate, ethyl *n*-butyrate, and methyl valerate.   W. G.

The Absorption Phenomena of Oxyhæmoglobin in the Grating Spectrum. OTTO SCHUMM (*Zeitsch. physiol. Chem.*, 1913, 83, 1—24).—The spectrum obtained by a diffraction grating is

spoken of as the natural spectrum, in contradistinction to that obtained by a prism. Careful measurements of the three bands (two in the visible, one in the ultra-violet region) are given, and the results figured in plates. Some variations occur even in the blood of the same species, and it is not possible to distinguish the oxyhæmo-globin of different animals by any such spectrum differences.

W. D. H.

Long- and Short-waved Absorption and Fluorescence Bands of the Carbonyl Group. M. GELBKE (*Jahrb. Radioaktiv. Elektronik*, 1913, **10**, 1—34).—The ultra-violet absorption of a number of ketones has been examined, the substances being dissolved for the most part in ethyl alcohol, although in a few cases the substances were investigated in the form of saturated vapour or dissolved in water or n-hexane. From a comparison of the short-waved absorption bands of acetone and its substituted derivatives, it is found that the acetone band, which has its maximum at $\lambda = 268\mu\mu$, is displaced in the direction of greater wave-lengths when one or more hydrogen atoms are substituted by alkyl, halogen, phenyl, nitroso- or carbonyl groups. In the case of alkyl substitution, the displacement of the maximum amounts to 5—$10\mu\mu$, whilst the effect of halogens, the phenyl, nitroso- and carbonyl groups is greater. The displacement of the band is accompanied by an increase in the absorption and also by a broadening of the band. From a comparison of acetone and *cyclo*hexanone it appears that the influence of ring formation is comparatively small.

In addition to the above-mentioned short-waved band, acetone shows a band with a maximum at about $\lambda = 365\mu\mu$, which extends from about $\lambda = 327\mu\mu$ into the visible spectrum. A similar band is also found in the substituted derivatives of acetone, and this it is which gives rise to the yellow colour exhibited by many such substances which contain the carbonyl group.

From a comparison of the absorption spectra of dimethyl diketone and methyl ethyl diketone with that of acetone, it is found that the short-waved band in the α-diketones is shifted about 5—$10\mu\mu$ in the direction of longer wave-lengths, and that the absorption is considerably intensified. In regard to the long-waved band, the shift exhibited by the two α-diketones amounts to about $30\mu\mu$ and the intensity is increased about forty times. In the case of β-diketones the intensification of the long-waved absorption band is not nearly so great as that observed for the α-diketones.

From a comparison of the spectra of methylheptenone, mesityl oxide, and phorone with that of acetone, it is found that both the short and long-waved bands are not appreciably shifted by a conjugated ethylene linking, although the intensity of the absorption increases very considerably in both cases. If the ethylene linking is not conjugated, but separated from the carbonyl group by two methylene groups, the absorption intensity of the short-waved band appears to be increased to a much smaller extent that when conjugation occurs.

The results of the spectrographic examination of the fluorescence bands

of acetone, dimethyl diketone, and oxalosuccinonitrile have been published previously (A., 1912, ii, 713), but a large number of other substances have now been examined in regard to the emission of fluorescent light when subjected to the action of intense ultra-violet radiation These observations show that the activity of the carbonyl group in this direction is quite general, fluorescence being exhibited by both mono- and di-ketones, and by both cyclic and acyclic compounds in which it occurs. It is thus proved that the faculty of fluorescence is by no means confined to ring compounds.   H. M. D.

Rotation Dispersion. ERNST DEUSSEN (*J. pr. Chem.*, 1913, [ii], 87, 96).—A correction. In reply to Tschugaev (this vol., ii, 3), the author admits that the rotations for mercury light recorded in previous papers (A., 1912, ii, 510, 1020) refer to light of wave-length $546\mu\mu$, and not $491 \mu\mu$.   F. B.

The Rotation Dispersion of Some Coloured Lactates. H. VOLK (*Ber.*, 1912, 45, 3744—3748).—Abnormal rotation dispersion of coloured asymmetric organic compounds, which has, hitherto, only been studied in the case of somewhat complicated substances (Grossmann, A., 1900, ii, 372, and Tschugaev, A., 1909, ii, 631), has now been observed with the copper, nickel, and cobalt salts of *l*-lactic acid. A maximum rotation is found in each case, in the region of selective absorption. Increase of temperature diminishes the rotation, but does not affect the character of the dispersion.

For the preparation of these salts, zinc ammonium *l*-lactate (Purdie, T., 1893, 63, 1143), which has a normal but comparatively high rotation-dispersion, is boiled with baryta water to expel ammonia and precipitate the zinc, and after removing the excess of barium hydroxide by means of carbon dioxide the filtrate is treated with the equivalent amount of the metallic sulphate and allowed to crystallise.

Copper l-*lactate*, $Cu(C_3H_5O_3)_2,1H_2O$, a light blue, crystalline powder, has a maximum rotation and absorption in yellow light; [M], calculated for lactic acid, falls from 18·5 in the green to 15·6 in the dark blue. *Nickel* l-*lactate*, $Ni(C_3H_5O_3)_2,4H_2O$, a light green powder, is remarkable in that it is *laevo*-rotatory in all parts of the spectrum; the maximum rotation, [M] = − 0·8, and strongest absorption are in the yellow.

Cobalt l-*lactate*, $Co(C_3H_5O_3)_2,2H_2O$, a light red powder, has maximum absorption for green light, in which [M] = 30; the rotation falls towards either end of the spectrum, and changes sign between light blue and dark blue.   J. C. W.

Sunlight. PAUL C. FREER and HARRY D. GIBBS (*J. Physical Chem.*, 1912, 16, 709—738).—The influence of sunlight on chemical and physiological processes is supposed by some to be greater in the tropics than in temperate climates. On the assumption that the difference lies in the intensity of the ultra-violet radiation, an investigation of the photochemical action of tropical sunlight should yield some information as to its probable physiological action.

The effect of sunlight in Manila in promoting the coloration of

a number of benzene derivatives, such as cresol and aniline, has been described from time to time by Gibbs. Since these reactions have large temperature-coefficients, and the temperatures of solutions exposed to the sun in Manila may attain 50°, Gibbs' experiments gave no certain indication that sunlight is abnormally active in the tropics.

Measurements of the total insolation in heat units made with the Ångström pyroheliometer at various latitudes indicate that the heat intensity varies but little from place to place. The intensity of violet and ultra-violet radiation is conveniently measured by the rate of decomposition of oxalic acid in presence of uranyl acetate. This reaction has a very small temperature-coefficient, and when used under standard conditions gives useful comparative results.

In Manila the average amount of oxalic acid decomposed in one hour during one year was 12·45%, the maximum being 17·8% and the minimum 1·15%. The average values obtained by other observers were as follows : Baguio (Philippine Is.) 14·2%; Honolulu, 13·9%; Kuala Lumpur (Malay States), 15·29%; Khartoum, 17·8% (using quartz dark); Washington, 11·9o%; Tucson (Arizona), 13·0%; Munich, 8·39%. When the sky is clear, the activity is almost the same everywhere, and the lower averages in the higher latitudes may be ascribed to the higher percentage of dull days.

Oxyhæmoglobin is converted by ultra-violet light into methæmoglobin which can be detected in the blood of rabbits which have died by exposure to the sun. Nevertheless, experiments in which rabbits, monkeys, and men of different shade were exposed to the sun seem to lead to the conclusion that the ill-effects are wholly due to the rise in blood-temperature and that the resistance of an individual depends largely on his opportunity for cooling by radiation, etc., and the perfection of his heat-regulating system of sweat glands; thus black, grey, and white rabbits, monkeys, and men, showed an increasing resistivity. Monkeys exposed to the sun in Manila died in less than two hours, the blood temperature rising almost 10°, but when the animals were kept cool by a fan, although exposed to the full radiation, including the ultra-violet, no ill-effects followed. The brain in these experiments was to some extent protected by the hair on the head.

R. J. C.

Photochemical Reduction of Copper Sulphate. CHARLES W. BENNETT (J. Physical Chem., 1912, 16, 782—785).—The author propounds the theory that the light which is absorbed by cupric sulphate solution tends to decompose it, so that a reducing agent might be found which, although without action in the dark, would precipitate copper when assisted by radiations of appropriate wavelength.

Experiments are cited to show that light reduces ammoniacal copper sulphate to cuprous oxide in presence of hydrazine hydrate, and that the precipitation of copper phosphide from 5% cupric sulphate solution by an ethereal solution of phosphorus (Mrs. Fulhame, 1794) is accelerated by the light from a carbon arc. In the latter case a quartz vessel was used.

R. J. C.

The First Stages in the Photolysis of Ethyl Alcohol, Acetaldehyde, and Acetic Acid. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1913, 156, 68—71).—Of the three substances studied. acetaldehyde is the only one which is acted on by sunlight ($\lambda > 0\cdot3\mu$), the alcohol and acid requiring radiations of shorter wave-length. There are four stages in the photolysis of acetaldehyde namely : (1) gaseous decomposition into carbon monoxide and methane (compare A., 1910, i, 543). (2) Polymerisation and subsequent evolution of hydrocarbons, such as ethane, etc. (compare A. 1910, ii, 814). (3) Formation of resinous products. (4) Conversion of the aldehyde into acetic acid. Only the first reaction is produced by initial ultra-violet rays, the three others requiring the mean or extreme rays.

The photolysis of ethyl alcohol consists fundamentally of the evolution of hydrogen and formation of acetaldehyde, which is then further decomposed (compare A., 1911, ii, 833). Acetic acid, on decomposition by the rays from an Heraeus lamp, gives a gaseous product containing carbon dioxide (44%), carbon monoxide (17%), and combustible gases (39%) (compare A., 1910, ii, 814). Water has no effect on the products of photolysis, but lessens the rate of the reaction.   W. G.

Photolysis of Different Complex Sugars (Bioses and Trioses) by Ultra-violet Rays. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1912, 155, 1506—1509. Compare A., 1912, ii, 1120).— A study of the decomposition of the bioses, maltose, lactose, trehalose and gentiobiose, and the trioses, raffinose, melezitose and gentianose, by ultra-violet rays of varying wave-length. In the case of the trioses no first stage of formation of a monose and a biose could be detected. After the first stage in the decomposition, the action was the same as in the case of the monoses (*loc. cit.*).   W. G.

The Radio-elements, the Periodic System, and the Constitution of the Atom. A. VAN DEN BROCK (*Physikal. Zeitsch.*, 1913, 14, 32—41).—This paper deals with recent work in the radioactive disintegration series and in the rare earth group, with the intra-atomic charge and theories of the constitution of the atom and their connexion with the periodic law in a manner unsuitable for abstraction.   F. S.

Evidence of Spontaneous Alterations of Concentration in Solutions and Gases. THEODOR SVEDBERG (*Physikal. Zeitsch.*, 1913, 14, 22—26. Compare A., 1912, ii, 905, 906).—The question is discussed as to whether the relative deviation of the number of α-particles produced in a volume element of a solution of a radio-active substance from the mean value should be theoretically greater than the corresponding relative deviation from the mean value in the case of the solid substance. It has been shown previously that the ratio of the mean deviations should be $\sqrt{2}:1$, and experimental observations indicate that this is approximately the case. Further arguments are

now put forward in support of the correctness of the above theoretical conclusion.

The question of the detection of spontaneous alterations in the concentration of solutions of other than radioactive substances is also examined with reference to the negative results which have been obtained up to the present. The author draws the conclusion that such changes cannot be detected by the methods of examination which are at present available.   H. M. D.

Excitation of γ-Rays by α-Rays. JAMES CHADWICK (*Phil. Mag.*, 1913, [vi], **25**, 193—197. Compare A., 1912, ii, 1025).—Further evidence is given that the impact of α-rays on metals of high atomic weight excites γ-rays. A tube, of such thin glass that the α-rays escape, containing radium emanation was surrounded with two concentric tubes of metals of widely different atomic weights, of thickness just sufficient to stop all the α-rays. The position of the two metals was transposed, and the ionisation with the two arrangements accurately compared by a balance method. Always when the metal of high atomic weight was next the emanation tube and bombarded by α-rays, the ionisation current was slightly greater than when the metal bombarded was of low atomic weight. The effect was much increased by filling the ionisation chamber with vapour, such as carbon disulphide or methyl iodide. The ratio of the ionisation in these vapours to that in air by X-rays of low penetrating power is much greater than for X-rays of high penetrating power, and it was to be expected that the γ-rays generated by α-rays would have a much lower penetrating power than the primary γ-rays, and that the part of the effect due to them would be greater in a heavy vapour than in air. If a thickness of light material was placed round the tube, sufficient to absorb the α-rays, the effect disappeared. That it was not due to very soft β-rays was proved by experimenting in a powerful magnetic field sufficient to coil up the β-rays and prevent them from reaching the metal. This did not cause any change in the effect. With outer tube of aluminium, the inner tube being of the following materials: gold, silver, copper, aluminium, paper; the relative ionisations in carbon disulphide vapour were respectively, 104·8, 102·5, 101·2, 100, and 99·7. This shows that the excitation of γ-rays by α-rays increases with the atomic weight of the material bombarded. A rough estimate of the coefficient of absorption of the excited γ-rays was 8 (cm.⁻¹ of aluminium).

In confirmation it has been shown, with A. S. Russell, that ionium and polonium, which give α-rays without β-rays, give γ-rays in amount sufficient to be studied in detail.   F. S.

Retardation of α-Particles by Metals. E. MARSDEN and H. RICHARDSON (*Phil. Mag.*, 1913, [vi]. **25**, 184—193. Compare Taylor, A., 1908, ii, 783; 1909, ii, 850).—The "air-equivalent" of a metal foil is the distance in cm. by which the range of an α-particle at 76 cm. and 15° is reduced in passage through the foil, and is, for materials of atomic weight greater than that of air, the less the less the velocity of the α-particle, or the nearer it is to the end of its range. This variation has been studied for the α-rays of radium-*C*

by a scintillation method, which offers advantages, only the fastest α-particles, that is, those which have not been scattered, being observed. A zinc sulphide screen is rigidly attached in the focus of the microscope, and is carried by the rack and pinion to any required distance from the source of α-rays. Between on a separate rack and pinion the foil is mounted, and the air-equivalent of the foil studied at various parts of the range of the α-particles. Tables are given for the variation of the air-equivalent, which is considerable, especially near the end of the path, with the range, and also a curve from which the air-equivalent of any thickness of foil (Au, Ag, and Al) at any part of the range can be deduced. A brightening of the screen, just outside the extreme range of the α-particles themselves, which is unaffected by a transverse magnetic field, was observed and is ascribed possibly to γ-rays excited by α-rays (see preceding abstract).

F. S.

Absorption of β-Rays. J. A. GRAY (*Proc. Roy. Soc.*, 1912, *A*, 87, 487—489).—Two experiments on the absorption of the β-rays of radium-*E* by paper show that the rays become more and more absorbable, practically none passing 56 sheets, weighing 8·77 mg. per $cm.^2$, the percentage transmitted by 5 sheets decreasing from 50 to 10.

These results are explained on the view that β-rays are both retarded and stopped by matter, and when the velocity of the surviving rays falls below the previous mean velocity, the exponential law can no longer hold.

F. S.

Similarity in Nature of *X*- and Primary γ-Rays. J. A. GRAY (*Proc. Roy. Soc.*, 1912, *A*, 87, 489—501).—The absorption of the primary γ-rays of radium-*E* and of the γ-rays excited in lead by the β-rays of radium-*E* is compared with the absorption of *X*-rays. The γ-rays of radium-*E* are absorbed somewhat similarly to characteristic secondary *X*-rays excited in silver. There is no discontinuity, with respect to absorption, between *X*- and γ-rays. Tin absorbs the γ-rays of radium-*E* to an abnormal extent, but for iron and gold compared with aluminium, the absorption is similar to that of the silver *X*-rays.

An investigation of the radiation reflected from radiators of various materials showed that the γ-rays of radium-*E* excite the characteristic *X*-radiation in silver, tin, barium, neodymium, and praseodymium. This furnishes the most definite proof possible that *X*-rays and γ-rays are of the same nature.

Lastly, the scattering of γ-rays of radium-*E* and of *X*-rays has been compared, and it is shown that the phenomena is similar both in magnitude and character for both radiations.

F. S.

Expansion Apparatus for Making Visible the Paths of Ionising Particles in Gases, and the Results Obtained with this Apparatus. CHARLES T. R. WILSON (*Jahrb. Radioaktiv. Elektronik*, 1913, 10, 34—35. Compare A., 1911, ii, 565).—The expansion apparatus and method of illuminating the condensed water droplets, described in the previous paper, have been improved in several

respects with the result that it has been possible to obtain photographs of the most rapidly moving β-rays, which show the droplets due to the individual ions. The greatly increased size of the cloud chamber in the new apparatus, not only enables the entire course of the longest-ranged α-particles to be registered, but its depth is such that horizontal beams of X-rays may be examined without any danger of interference from the proximity of the roof or base of the chamber. The photographic records obtained under the new conditions are, moreover, much more distinct than those given by the earlier form of apparatus.

In regard to the α-particles, the photographs show that these move along paths which are approximately rectilinear, except for the last 2 mm., where there is a very marked change in direction. Apart from this sudden and pronounced change at the end of the range, there is, however, in many cases a small and gradual change in direction over the greater part of the course, and the photographs thus afford evidence of both single and compound scattering.

The photographs of the β-rays indicate that the ions are formed in pairs over a considerable portion of the path, but that at certain points closely packed groups of twenty or thirty ions are produced. The occurrence of these groups of ions is regarded as evidence of the emission by the atoms of secondary corpuscles which possess sufficient energy to produce ionisation over a small range. In opposition to the α-rays, the β-rays never exhibit sudden changes in direction, although the slow change due to compound scattering is clearly shown, provided the velocity of the rays is not too large.

The X-ray photographs show that β-rays proceed from points in the paths of the X-rays beam. Apart from this production of β-rays, the X-rays appear to give rise to no effect which is photographically registered on the plates. Corresponding with the heterogeneity of the X-rays, it is found that the paths of the individual β-particles vary considerably in length. The rays appear to show both simple and compound scattering, although the latter effect appears to be the much more frequent and characteristic type. The emission of the β-rays appears to be uniformly distributed in all directions, and no evidence of any dependence on the direction in which the X-ray beam is propagated has been obtained.

In the case of both the β-ray and X-ray photographs, it has been possible to ascertain approximately, by counting the droplets, the number of ions which are produced per centimetre of path.

H. M. D.

Ionisation Produced by β- and γ-Rays at High Pressures. D. C. H. FLORANCE (*Phil. Mag.*, 1913, [vi], 25, 172—183).—The absorption and ionisation produced in air at high pressure with the β-rays of uranium-X and with the secondary β-rays generated by the γ-rays of radium-C have been studied by means of a special cylindrical ionisation vessel with pressures of air up to 80 atmospheres. Complete saturation could not be obtained, even with a field of 1800 volts per cm., the shape of the curves being similar to those obtained with α-rays. There is for constant voltage a constant ratio for the ionisa-

tion currents at any two pressures, and although saturation is not attained, the ionisation currents are proportional to the intensity of the radiation at different pressures. The experimental value found for μ(cm.$^{-1}$ of air at atmospheric pressure) for the β-rays of uranium-X was, for plates 7 cm. diameter and 1 cm. apart, 0·04, but the true value for a parallel beam of β-rays was deduced to be 0·007, in agreement with the value of μ in solids. The values for the emergent and incident β-rays produced by γ-rays of radium-C were 0·046 and 0·056, and they appear to be independent of the nature of the material in which they originate. With plates 1 cm. apart the part of the ionisation due to β-rays originating in the gas is negligible at atmospheric pressure and 25% of the total ionisation at 80 atmospheres.

F. S.

Recombination of Ions Produced by Röntgen Rays. S. J. PLIMPTON (*Phil. Mag.*, 1913, [vi], 25, 65—81 ; *Amer. J. Sci.*, 1913, [iv], 35, 39—53).—The value of a, the coefficient of recombination of the ions in the equation $dn/dt = -an^2$, was determined by ionising the gas between two parallel plate electrodes by a single flash of X-rays, restricted so as not to fall upon the plates, allowing the ions produced to recombine in absence of any external field for small intervals of time, regulated and determined mechanically, and then by sudden application of a field driving the residual ions to the electrodes and so evaluating their numbers. In this way the effect of ionic diffusion can be greatly reduced, corpuscular radiation from the metal plates eliminated, uniformity of X-rays secured, and the initial stages of recombination studied. The results revealed, especially for carbon dioxide, an initial value of a relatively large, but decreasing and becoming constant after intervals usually of about one-third of a second. This is explained by initial recombination of the pair of ions formed before they have moved by diffusion out of their range of mutual influence, and the high value in carbon dioxide and the slower rate at which the normal value is attained are ascribed to the slower diffusion in this gas than in air. If a field acts during the flash, ceasing to act simultaneously with the cessation of the flash, the final value of a is not affected, but the initial value is decreased. A table is given of the absolute values of a at various time-intervals from the cessation of ionisation for air, carbon dioxide, sulphur dioxide, methyl iodide, ethyl chloride, ethyl bromide, and ethyl ether at various pressures. For air, the initial value of a/e, when e is the atomic charge, is 11,540, and the final value, 3960.   F. S.

Further Experiments on the Mobility of the Positive Ions at Low Pressures. GEORGE W. TODD (*Phil. Mag.*, 1913, [vi], 25, 163—171. Compare A., 1912, ii, 245, 1050).—The experiments have been repeated with a larger apparatus in order to obtain information at lower pressures, at which it was formerly suggested sub-molecular particles might constitute the positive ions. The new experiments show nothing like the enormous increases in the mobilities previously observed, but indicate that below the

pressure of 1 mm. the mobilities vary with the period of alternation of the field when the period is high (above 150~).　　F. S.

Combination of Hydrogen and Oxygen in the Presence of Heated Platinum and Carbon. J. R. THOMPSON (*Physikal. Zeitsch.*, 1913, **14**, 11—15).—Experiments have been made with the object of ascertaining whether there is any connexion between the temperature at which hydrogen and oxygen begin to combine in contact with heated platinum or carbon, and that at which these begin to emit negatively charged particles.

The platinum spiral or carbon filament was contained in a cylindrical glass tube which could either be exhausted or connected with a supply of the gas mixture. The temperature of the spiral could be gradually raised by means of a regulated current from an accumulator battery and a voltmeter placed across the ends of the wire enabled the resistance to be measured. An aluminium cylinder surrounding the heated wire was connected with one pair of quadrants of a Dolezalek electrometer, and permitted the measurement of the electrical effect at gradually increasing temperatures.

From observations made when the tube was highly exhausted and when hydrogen and oxygen were admitted at different pressures measured by the manometer, it has been found that in the case of platinum and of carbon, the temperature at which the emission of negative particles is first observed is within the limits of experimental error identical with the temperature at which combination occurs between the hydrogen and oxygen. In all cases the explosive combination of the gases was found to be accompanied by large ionisation currents, but these could not be measured. The actual temperatures at which the two effects occur were not measured, the temperature being measured in terms of the resistance of the wire as ascertained from the readings of the voltmeter and ammeter. The influence of the gas on the observed resistance was allowed for by means of a series of readings with the apparatus when the heated wire was in contact with air at different pressures.

Preliminary observations show also that combination of hydrogen and oxygen occurs if the platinum wire is subjected to the action of a beam of X-rays. The combination occurs more readily if the percentage of hydrogen is less than 10.　　H. M. D.

Investigation of the Spectrum of Ionium. ALEXANDER S. RUSSELL and R. ROSSI (*Proc. Roy. Soc.*, 1912, *A*, **87**, 478—484).— The ionium preparation employed (Boltwood, A., 1911, ii, 359), from measurements of the number of α-particles emitted, should contain 16% of ionium, if the period of that substance is 100,000 years, the remainder being thorium oxide. After chemical purification of the ionium-thorium preparation by various methods, its arc spectrum between the wave-lengths 3800 to 5000 was photographed in juxtaposition with that of a pure thorium oxide preparation, in the first order by a Rowland's grating of 21·5 feet radius giving a dispersion of 2·6 Ångström units per mm. The spectrum was identical with that of pure thorium save for the presence of five of the stronger lines of

scandium, the amount of which in the purified preparation was esti-
mated as three or four parts per thousand. It was found that an
admixture in thorium oxide of 1% of cerium oxide could easily, and
1% of uranium oxide could just, be detected spectroscopically. The
obvious conclusion is that ionium cannot be present in the preparation
to the extent of more than 1 or 2%, and that its period of average life
cannot be more than 12,000 years.

This result is consistent with the estimate given by Soddy of at
least 100,000 years, only if at least one unknown product of long life
intervenes between uranium and radium. On the other hand, the
period deduced from the range of the α-rays, 200,000 years, is not
consistent with the result obtained unless the α-rays of ionium are
exceptional. It is possible that ionium has no arc spectrum in the
region investigated, although this is improbable, or that ionium and
thorium have identical spectra, as they have identical chemical
properties.

In a note, the paper on the same subject by Exner and Haschek
(*Sitzungsber. K. Akad. Wiss. Wien*, 1912, **121**, iia, 1075) with the same
result is referred to, the ionium in the Austrian preparation being
estimated as two-thirds of that in the one employed.   F. S.

**The Solid Radioactive Disintegration Products Suspended in
the Atmosphere.** K. W. FRITZ KOHLRAUSCH (*Physikal. Zeitsch.*, 1912,
13, 1193).—Certain corrections are discussed in the methods employed
in the measurement of the solid radioactive products in the atmo-
sphere, and new expressions more in accord with recent work are
deduced. For the determination of the amount of radium-A in the
air by passing the air at a suitable velocity for a known time through
a tubular condenser with inner electrode negative, and measuring the
ionisation current at the end due to the active deposit on the inner
electrode, tables are given showing the ratio of the effect for any time
of aspiration to that for an indefinitely long time. In the second
place the effect of the thorium products in the air is taken into
consideration.   F. S.

**Electro-chemistry of Extremely Dilute Solutions, in Parti-
cular of Radioactive Substances.** KARL F. HERZFELD (*Physikal.
Zeitsch.*, 1913, **14**, 29—32).—If a metal plate is immersed in a solution
of one of its salts which contains a mixture of two radioactive
substances in a definite ratio, then, according to the experiments of
Hevesy (A., 1912, ii, 414), the ratio in which the radioactive metals
separate on the metal plate is dependent solely on the potential
difference at the contact surface of the metal and its salt solution.
This observation is contrary to what would be expected on the basis of
Nernst's formula for the equilibrium at the surface. The discrepancy
may be explained if it is assumed that the quantity of deposited
radioactive metal in the equilibrium condition is not sufficient to
form a complete molecular layer. If P' denotes the solution
pressure of the radioactive metal, p_0 the osmotic pressure of the
amount initially present in the solution, and π the pressure correspond-
ing with the metal deposited in the equilibrium condition then the
cathode potential E, will be related to these quantities by the equation

$E = RT \log P' \pi / (p_0 - \pi)$. The application of this equilibrium equation to two radioactive substances present in the solution leads to results in agreement with the observed facts. In regard to the variation of the ratio of the deposited metals with the magnitude of the potential at the metal surface, the formula gives a curve which is also of the same type as that representing the experimental data.   H. M. D.

Electrical Excitation in the Splashing of Liquids (Ballo-Electricity). CHRISTIAN CHRISTIANSEN (*Ann. Physik,* 1913. [iv], 40, 107--137).—An account is given of experiments in which the electrical phenomena associated with the incidence of liquid spray on a solid surface have been investigated. By means of a current of air under constant pressure, the liquid under examination is made to issue from a small aperture in the form of a fine spray which impinges on a plate or on the walls of a tube of the solid substance to be investigated. In most of the experiments a platinum disk or tube was employed, and this was connected by a wire with the liquid in the supply reservoir, and also with one pair of quadrants of an electrometer, the opposite pair being earthed.

The magnitude of the electrical effect obtained when distilled water is sprayed was found to vary very considerably with the sample of water employed. In searching for the cause of these irregularities, it has been found that contact of the water with any substance, such as glass, paper, wool, silk, oils, etc., which has been exposed to the air for a considerable time, gives rise to a greatly increased electrometer deflection. The influence of electrolytes on the hallo-electric effect is relatively very small, and the much greater influence of contact with the above-mentioned substances is supposed to be due to the condensation of radioactive substances on the air-exposed surfaces.

The deflections obtained with aqueous solutions of acids, bases, and salts, and the influence of dilution have been examined, with the result that the chemical nature of the electrolyte appears to be of little importance in connexion with the phenomenon. According to the magnitude of the electrical effect it is possible to divide aqueous solutions into two groups. When solutions belonging to these different groups are mixed, it is found that the ballo-electric activity of the mixed solution is very much greater than that of the components. As an example, it may be mentioned that if equal volumes of molar solutions of ethyl alcohol and potassium chloride are mixed together, the effects obtained with the mixed solution was 7·0, whilst that given by the alcohol solution was 0·9, and by the potassium chloride 0·1. Several such mixtures have been investigated in such a way as to obtain comparative numbers for related substances belonging to the two above-mentioned ballo-electric groups.

Other experiments show that the effect varies with the nature of the solid surface on which the liquid spray impinges. With a distilled water spray, platinum glass and ivory become positively charged, whilst paraffin becomes negative. In the case of wax and shellac, the solid is at first negatively charged, but after prolonged action the sign of the charge becomes reversed. The most constant results are obtained with a platinum surface.   H. M. D.

Dielectric Constants of Dissolved Salts. II. PAUL WALDEN (*Bull. Acad. St. Pétersbourg*, 1912, [vi], 1055—1086).—Investigations similar to those previously made with chloroform solutions (compare A., 1912, ii, 421) have been carried out with solutions in dichloromethane (dielectric constant, 8·3) and in ethyl formate (dielectric constant, 8·2), which differ from chloroform in giving measurable ionic dissociation of the salts employed (*loc. cit.*). Further, ethyl formate is a solvent of an entirely different type, so that its use opens up the possibility of studying the chemical rôle of the atoms constituting the solvent.

As with chloroform so also with dichloromethane, the dissolution of the salts is accompanied by a considerable increase in the dielectric constant of the solvent. Further, the dielectric constants of the salts, calculated by means of Philip's, Bouty's, and Silberstein's formula, are mostly very high, the greatest values being obtained with the first of these formulæ. In dichloromethane, the value of the dielectric constant of any salt is much higher than in chloroform. This constant also increases with the complexity of the salt and, according to Philip's formula, has the values: $NHEt_2,HCl$, 88; NEt_3,HCl, 390, and NEt_4Cl, 1980; the numbers for the corresponding nitrates are 71, 425, and 1365 respectively.

For one and the same salt at equal dilutions, the molecular conductivity is from ten to thirty times as great in dichloromethane as in chloroform, and whilst in the latter solvent it diminishes rapidly and continuously as the dilution increases, in the former a minimum is observed at a certain dilution. The conclusion is drawn that the ions formed from the salt are able to raise the dielectric constant of the solution and also the dissociating power of the solvent.

Ebullioscopic measurements show that the salts have different molecular magnitudes in these two solvents, these being, for NEt_4Cl, M_6 in chloroform and M_2 in dichloromethane, and for NEt_3,HCl, M_2 and $M_1 - M_2$ respectively. The increased values of the dielectric constants in dichloromethane may be due partly to this depolymerisation and partly to a specific catalytic influence of the solvent.

The chemical process of salt-formation by the conjunction of two neutral constituents ($NEt_3 + EtBr$, etc.) is expressed physically in a reconstruction of the dielectric properties of these constituents in such a way that the new product shows a dielectric constant which is about six, thirteen, or eighteen times that calculated additively for secondary amine, tertiary amine, and tetralkylammonium salts respectively.

Calculation by means of the Clausius-Mosotti equation, $x = (K-1) (K+2)$, where x represents the fraction of the total volume actually occupied by the molecules, shows that these salts are the best electrolytes for which x approaches the value 1.

Not only is the general behaviour of ethyl formate as regards the alteration of the dielectric constants of dissolved alkylamino-salts similar to that of dichloromethane, but the actual values of these constants are very nearly equal with the two solvents. Sodium iodide and lithium bromide are characterised by extremely high dielectric

constants in ethyl formate, the values obtained being 5595—6820 and 4760—5300 respectively according to Philip's formula ; calcium iodide shows a much smaller value (1540), and mercuric chloride one still smaller (490) ; thus, the dielectric constant of these salts diminishes with their capacity to dissociate.

The results obtained with solutions of salts in the strongly-ionising solvents acetone, acetylacetone, acetonitrile, and propionitrile confirm the conclusion that if the dielectric constant of the medium remains constant, the formation of ions increases the ionising tendency and the degree of electrolytic dissociation of the salt.

Certain anomalies exhibited by solutions are discussed in connexion with the increases produced in the dielectric constants, and hence in the ionising power of solvents by the dissolution of electrolytes. It is pointed out that this phenomenon must be taken into account in considering deviations from the law of mass action (Ostwald's dilution law), the rôle of neutral salts, the disagreement of salts dissolved in media having feeble ionising actions with the requirements of the theory of Arrhenius, etc., since by it, as well as by the other well-known factors, the degree of electrolytic dissociation is appreciably altered.   T. H. P.

Behaviour of Carbon on Electrical Pulverisation. CARL THOMAE (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 268—269).—If a continuous current of 3—4 amperes at 220 volts is passed between retort-graphite electrodes immersed in pure water, the liquid remains quite transparent, but if a very small quantity of sodium hydroxide is added, a dark brown colloidal solution is obtained. The solution is stable, and may be boiled without change, but the addition of hydrochloric acid or sodium chloride gives rise to a black precipitate. Similar results were obtained with arc-lamp-carbon electrodes.

H. M. D.

Theory of the Electrical Synthesis of Colloids. CARL BENEDICKS (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 263—268).—A criticism of the views expressed by Kutscherov (A., 1912, ii, 1148) in connexion with the interpretation of the phenomena of electrical pulverisation. In opposition to the theory that the process is partly electrochemical in nature, the author maintains that the observations can be adequately explained on the assumption that the action is entirely thermal in character.   H. M. D.

The Mobility of the Bromide Ion in Water. CARL DRUCKER, M. TABLE, and L. GOMEZ. (*Zeitsch. Elektrochem.*, 1913, 19, 8—11).—The transport numbers of tribenzylmethylammonium bromide were determined at 20° by the usual method, employing a zinc anode and a platinum cathode. As a mean of many experiments, the value $n_a = 0.775$ was obtained. To calculate the mobility of the bromine ion from this figure, the conductivity values at 18° were used (Drucker, A., 1912, ii, 732). The temperature-coefficient of the conductivity was determined, and found to be 0.022 between 18° and 25°, and from these data the mobility of the bromine ion is 65.5. This value is much

lower than that obtained by Kohlrausch (67·0), and affects the conductivity, at infinite dilution, of potassium bromide, making it 129·8 instead of 132·6, as extrapolated by Kohlrausch. Possible sources of error in the Kohlrausch value are discussed. It is shown, on calculating the degree of dissociation of potassium bromide from the new value, that it obeys the Ostwald dilution law up to 0·01n. The authors assert that, very probably, all strong electrolytes obey the dilution law up to this concentration.   J. F. S.

Investigation of the Chemical Reactions Taking Place **at the Cathode and Anode During the Electrolysis** of **Simple Salt Solutions.** J. HAMILTON PATERSON (*Proc. Univ. Durham Phil. Soc.*, 1912, 4, 187—220).—The author describes a small electrolytic cell which allows of the microscopic examination of the deposits formed on the electrodes during electrolysis. Experiments made with simple salts (chlorides, nitrates, or sulphates) of a number of metals have shown that it is possible to obtain from cobalt, nickel iron, zinc, cadmium, manganese, and possibly lead salts, either the pure metal or the hydroxide, deposited on the cathode. In the case of cobalt, the film of hydroxide has a deep blue colour, but the moment the current stops it turns green ; the composition of the green compound corresponds with the formula $Co(OH)_2, H_2O$.

The conditions of concentration and current density affecting the production of these substances has been noted, and it has been found that the dilution necessary to produce the hydroxide increases and the limit of current strength decreases as we proceed along the list of metals in the order given.

The hydroxide of the metal is not produced as a secondary reaction of the metal deposited on the cathode, but is a precipitate from the electrolyte in the cathode area.   F. B.

The Constitution of Water and the Thermal Variation of **its Magnetisation.** AUGUSTE PICCARD (*Compt. rend.*, 1912, 155, 1497—1499. Compare this vol., ii, 17).—From a study of the change in the coefficient of magnetisation of water on solidification at 0°, and a comparison of the curves representing respectively the variation in density and magnetisation coefficient with respect to temperature, the author draws the conclusion that, in water at the ordinary temperature, there are two different substances in equilibrium.   W. G.

New Thermo-regulator for Instantaneous Adjustment to any **Given Temperature.** R. FÄNDER (*Chem. Zeit.*, 1913, 37, 40).—The regulator bears much resemblance to that of Reichardt, but differs in having the adjusting screw on the lower half of the capillary tube, the upper half of the tube being graduated from 30° to 100°.

The regulator is set by immersing it in a water-bath at any temperature, and adjusting the mercury column so that the readings on the capillary tube correspond with those of a thermometer in the bath for about a minute. The mercury is then raised or lowered to the graduations corresponding with the desired temperature, and the regulator is ready for use.   H. B. H.

The **Expansion Coefficient of Graphite.** ARTHUR L. DAY and ROBERT B. SOSMAN (*J. Ind. Eng. Chem.*, 1912, **4**, 490—492).—Contains sketches of the apparatus employed by the authors for measuring the expansion coefficient of graphites, whilst the results obtained are demonstrated in tables and curves. From the wide divergence in expansion coefficients obtained, the conclusion is drawn, contrary to the views of Le Chatelier and Wologdine (A., 1908, ii, 177) and in harmony with those of Arsem (A., 1912, ii, 250), that there must be some fundamental difference between the various forms of graphite.   F. M. G. M.

Volume Changes of Amalgams. J. WÜRSCHMIDT (*Ber. Deut. physikal. Ges.*, 1912, **14**, 1065—1087).—The influence of temperature on the thermal expansion of a number of amalgams has been examined with the aid of a special type of dilatometer. The curves obtained by plotting the coefficient of expansion as a function of the temperature exhibit very sharp maxima at definite temperatures. In the case of the tin, lead, and cadmium amalgams, which according to Puschin (A., 1903, ii, 212) consist of solid solutions, these temperatures are identical with the melting points of the alloys. On the other hand, the zinc amalgams, which consist of mechanical mixtures of the components, exhibit the maximum expansion at temperatures between 50° and 70°, which are very much lower than the melting points of the alloys. In regard to the nature of the expansion temperature curve, sodium amalgam resembles the corresponding tin, lead, and cadmium alloys, but differs from these in that the volume changes with time when the temperature is kept constant.   H. M. D.

Thermal Conductivity of the Metals and its Relation to Their Other Properties. STEFANO PAGLIANI (*Nuovo Cim.*, 1912, [vi], **4**, ii, 482—497).—The author gives a table showing the coefficients of thermal conductivity, the specific heats and the densities of a number of metals, the material being derived from published results of various workers. By a comparison of other published data, he shows that the metals can be arranged in a series, in which increased conductivity and reflecting power are associated with decrease of emissive power, and that these properties also fall within the regularity of the periodic law.   R. V. S.

Theory of Specific Heats. MAX BORN and TH. VON KÁRMÁN (*Physikal. Zeitsch.*, 1913, **14**, 15—19).—Reference is made to a previous paper (*ibid.*, 1912, **13**, 297), in which the discrepancy between the observed specific heats of solid substances at low temperatures and the values calculated from Einstein's formula has been eliminated to a large extent by means of a modified specific heat formula. The theory on which this is based is compared with the theory advanced by Debye (A., 1912, ii, 1134), and it is shown that the approximation formula proposed by Debye for the calculation of the atomic heats of solid non-atomic substances can be deduced from the general formula given by the authors. In the case of anisotropic substances, the approxima-

tion formula is inapplicable, and the general formula referred to must be employed in the calculation of the specific heats.   H. M. D.

Specific Heat of Certain Elements at Low Temperatures. TADEUSZ ESTREICHER and M. STANIEWSKI (*Bull. Acad. Sci. Cracow*, 1912, 834—841. Compare A., 1911, ii, 16).—The authors have determined the mean specific heats of bromine, iodine, sodium, potassium, and manganese over the temperature intervals $-190°$ to $18°$ and $-18°$ to $18°$. The mixture method was employed with water or toluene as calorimetric liquid. The specific heat of toluene at the ordinary temperature was found to be $0·4015 \pm 0·0003$ cal.

From the observations, the following average specific heat values are deduced: bromine $0·07016$ ($-190°$ to $-18°$); iodine $0·0454$ ($-191°$ to $-80°$), $0·04852$ ($-80°$ to $17°$); sodium $0·2478$ ($-191°$ to $-80°$), $0·2714$ ($-80°$ to $17°$); potassium $0·1551$ ($-191°$ to $-80°$), $0·1677$ ($-80°$ to $18°$); manganese $0·08203$ ($-188°$ to $-79·2°$), $0·10906$ ($-79·2°$ to $15°$). These values agree in general very well with the numbers obtained by Koref (A., 1911, ii, 964).   H. M. D.

Measurement of the Specific Heat of Solid Substances at High Temperatures. MARCELLO VON PIRANI (*Ber. Deut. physikal. Ges.*, 1912, 14, 1037—1054).—Three methods are described by means of which the true specific heats of different metals have been determined at high temperatures.

In the first method, the apparatus consists of an insulated electrically heated tube furnace, the temperature of which is adjusted to that at which the specific heat measurement is to be made. Inside this is a much smaller tube furnace, the temperature of which is measured by means of a thermo-couple. If a quantity of electrical energy, measured by a watt-meter, is passed through the coils of the inner tube during time t, its temperature will be raised by a small amount, $\Delta\theta$, which is measured by the couple.

Under exactly similar conditions, the energy required to produce the same rise of temperature when the inner tube is filled with the substance under examination is determined. From the data thus obtained the specific heat of the substance may be calculated.

The two other methods are somewhat similar and depend on the fact that when a conducting substance is heated electrically to a high temperature in a vacuum, the electrical energy communicated is lost almost entirely in the form of radiant energy. If the supply of electrical energy is increased for a short interval of time, the temperature will increase to an extent determined by the specific heat of the substance and by the increased amount of radiation. Since the latter case can be determined by experiments in the stationary condition it is obvious that the measurement of the extra electrical energy and of the consequent rise in temperature will afford a means of obtaining the specific heats of the metals at very high temperatures. The specific heats of tantalum and tungsten have been measured in this way at temperatures between about $350°$ and $1400°$. Data are also recorded for iron between $110°$ and $970°$. The curve showing the relationship between the specific heat of iron and the temperature is

very irregular, showing a very decided maximum at about 720°, and a sharp minimum at about 790°. No evidence of this minimum has been obtained in previous high-temperature measurements.

H. M. D.

Measurement of Specific Heats of Solid Substances at High Temperatures. ALFRED MAGNUS (*Physikal. Zeitsch.*, 1913, 14, 5—10).—The measurements were made with a form of calorimeter similar to that used by Nernst, Koref, and Lindemann (A., 1910, ii, 263), but in order to diminish the influence of the heat losses incurred in the introduction of the heated substances into the calorimeter, its capacity was increased about fifty times. The block of copper weighing 22 kilograms was provided with a conical shaped central cavity for the reception of the heated substance which was contained 'n a conical silver tube fitted with a stopper. The rise in temperature if the copper calorimeter was measured by means of a battery of i0 iron constantan thermocouples, half the junctions being ituated in deep holes in the block of copper and the other half in the vater-bath surrounding the Dewar vessel containing the copper block. Data representing the mean specific heats between the room temperaure and 100°, 270°, 550°, and 750° have been obtained, the substances examined being quartz, amorphous silica, magnesium oxide, calcium oxide, zinc oxide, lead oxide, sodium and potassium chlorides, sodium ind potassium bromides, and calcium carbonate.

The molecular heats appear to be in satisfactory agreement with those arrived at by recent workers at lower temperatures, continuous curves being obtained when the available molecular heats are plotted as a function of the temperature. The values for sodium chloride, potassium chloride, and potassium bromide are also in agreement with those calculated from the equation $C_p = C_v + ACp^2T$, in which $A = 2.7$, 2.7, and 3.3×10^{-5} for the three salts respectively.   H. M. D.

Investigations on Specific Heat. VI. Calculation of Atomic Heats. WALTHER NERNST and F. A. LINDEMANN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1912, 1160—1171. Compare A., 1911, ii, 464, 964, 1059).—On the assumption that a vibrating atom gives rise to a continuous spectrum corresponding with a continuous series of component vibrations, Debye (A., 1912, ii, 1134) has obtained a modified Einstein formula for the specific heat of a monatomic element. This has been applied in the calculation of the atomic heats of aluminium, copper, silver, diamond, potassium and sodium chloride at different temperatures, and the results are compared with the experimental data. This comparison shows that the new formula agrees better with experiment than either of the older formulæ of Einstein and of Nernst and Lindemann.

The available specific heat data indicate that two groups of elements may be distinguished. In the one group, the variation of the specific heat with the temperature can be satisfactorily represented by means of Debye's formula, whilst the substances in the other group are characterised by an appreciably less rapid fall in the specific heat with falling temperature than is required by the formula. Crystalline

elements belonging to the first group are probably monatomic, whilst those of the second group are probably polyatomic. The fact that potassium and sodium chloride behave like monatomic substances is attributed to the approximate equality of the vibration frequencies of the component atoms. H. M. D.

Investigations on Specific Heat. VII. Calculation of Chemical Affinities. WALTHER NERNST (*Sitzungsber. K. Akad. Wiss. Berlin*, 1912, 1172—1176).—The effect of the substitution of Debye's formula for the specific heat in place of that used by Nernst and Lindemann is considered in reference to the application of the author's heat theorem to the calculation of chemical affinities. Tables are given which indicate the magnitude of the correction factors for a series of vibration frequencies. H. M. D.

The Polymerisation of Substances at Low Temperatures. JACQUES DUCLAUX (*Compt. rend.*, 1912, 155, 1509—1511. Compare this vol., ii, 18).—A mathematical paper in which the author shows that the value of $\int_{T_0}^{T_b} \frac{dQ}{T}$, where dQ is the quantity of heat necessary at each temperature, T, to produce the modification studied, T_0 the absolute zero, and T_b is the absolute boiling point of the substance, is a constant for all substances and equal to 42 or twice the value of the constant in the Pictet-Trouton law, obtained by dividing the molecular heat of vaporisation by the temperature of vaporisation. The values are given as calculated for ten substances, the specific heat of which has been completely studied. W. G.

The Liquid Condition (Correction). WILLIAM C. McC. LEWIS (*Zeitsch. physikal. Chem.*, 1913, 81, 626—628. Compare A., 1911, ii, 855).—The author shows that the expression $L = -Ta/\rho\beta$ has only an empirical meaning, and he develops from thermodynamical principles the expression $l = -Ta/\beta$, in which l is the latent heat of expansion, that is, the amount of heat which must be added to a system to cause an increase in volume of one unit whilst the temperature is kept constant, a is the coefficient of expansion, and β the compressibility. The expression only holds for homogeneous systems, that is, either entirely liquid or entirely gaseous. The author has calculated the values of l for a number of liquids, and finds that its value is of the same order as the latent heat of vaporisation, from which he draws the conclusion that the region of molecular attraction must be of the same order as the mean distance of the molecules from one another, that is, about 10^{-8} cm. J. F. S.

Simple Method for Determining the Melting Point of the Less Fusible Substances. ERN. HAVAS (*Chem. Zeit.*, 1912, 36, 1438).—The author recommends a modification of the mercury method, in which the substance, of which the melting point is to be determined, is placed in small quantity on the surface of mercury,

which is gradually heated. The mercury is replaced by an alloy of 2 parts of tin and 1 of lead (ordinary soft solder), and melting points up to 450° can readily be determined.　　　　　　　　　T. S. P.

Melting Point of Fire Bricks. C. W. KANOLT (*Tech. Papers, Bur. Stands.*, 1912, No. 10, 1—17).—The melting point was taken as the lowest temperature at which a small piece of the brick could be distinctly seen to flow. An electric vacuum furnace was used, and the melting points of fifty-four samples of fire brick, including fire-clay, bauxite, silica, magnesia, and chromite bricks were determined, as well as the melting points of the following materials important in the manufacture of fire brick: kaolin, 1740°; pure alumina, 2010°; bauxite, 1820°; bauxite clay, 1795; chromite, 2180°.　　　　　　T. S. P.

Pressure-temperature Diagrams for *p*-Azoxyanisole and *α*-Naphthylamine. NICOLAI A. PUSCHIN and I. V. GREBENSCHTSCHIKOV (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1728—1736).—These diagrams have been investigated by the manometric method.

Up to pressures of 1088 kilograms per sq. cm., the melting point of *p*-azoxyanisole is a linear function of the pressure, and is expressed by the formula $t_p = 135·9° + 0·03949p$. Hulett, whose measurements were confined to the region 1—300 atmospheres, found the value 0·0486 for the pressure-coefficient of the melting point (A., 1899, ii, 468), this differing considerably from the authors' value, 0·0395. A possible bending of the melting-point curve at higher pressures, such as occurs with the great majority of other substances, has not been investigated. The transition point from the crystalline state to the liquid-crystalline condition varies linearly with the pressure as far as 2000 kilograms per sq. cm., and is expressed by $t_p = 117·3° + 0·02560p$ (Hulett, *loc. cit.*, found $dT_2/dp = 0·0320$). Increase of the pressure from 2000 to 2645 kilograms per sq. cm. is accompanied by increasing divergence of the transition point from the rectilinear curve, this behaviour being similar to that of the melting points of substances crystallising with diminution of volume.

The considerable difference between the pressure-coefficients of the melting and transition points of *p*-azoxyanisole and the rectilinear character of the curve connecting melting point and pressure up to 1088 kilograms per sq. cm. are regarded as contradictory to Ostwald's assertion (*Lehrbuch der allgemeinen Chemie*, 2nd Edition, II, 2, 392) that, with liquid-crystalline substances, small values for the change of volume on melting and for the heat of crystallisation readily become zero at pressures slightly in excess of that of the atmosphere; or, in other words, that with liquid crystals, the critical point for liquid-to-crystals can be realised experimentally.

For pressures up to 3000 kilograms per sq. cm., the melting point of *α*-naphthylamine is nearly a linear function of the pressure, and is given by: $t_p = 48·5° + 0·01723p — 0·000000555p^2$. The value, 0·0168, for dT/dp from 1 to 500 kilograms per sq. cm. differs considerably from the value, 0·0200, found by Hulett (*loc. cit.*). The authors' results do not agree with those of Damien (*Compt. rend.*, 1891, 112, 785), which would indicate a maximum for the temperature-pressure

curve of α-naphthylamine at a pressure of 83 atmospheres. The
equation given above shows that a maximum may be expected at
about 182° (15500 kilograms per sq. cm.), so that at higher tempera-
tures and pressures crystalline α-naphthylamine would be incapable of
existence.   T. H. P.

Thermal Analysis. T. VAN DER LINDEN (*J. Chim. phys.*, 1912, 10,
454—466).—The paper gives an account of the theory of the method
largely used by Holleman and his pupils, of estimating the com-
position of mixtures from freezing-point data alone.

In a homogeneous liquid with n components, which form no com-
pounds or mixed crystals at atmospheric pressure, the total weight
of the system being 100, the degrees of freedom $= n$, of which $(n-1)$
are variable concentrations and the remaining one is the temperature.
On cooling the system, one of the n constituents crystallises out at the
first freezing point, and as there are now two phases, the degrees of
freedom are reduced to $(n-1)$. The first solidifying temperature is
therefore fixed by the proportions of the $(n-1)$ constituents remain-
ing in the melt. Similarly the second solidifying point is a function
of the $(n-2)$ constituents remaining, and so on ; thus the $(n-1)$th
freezing point is independent of the proportions of the $(n-2)$ con-
stituents already solidified, but dependent on the ratio a of the two
constituents remaining in the melt, that is, the $(n-1)$th freezing
point $= f(a)$. This function is represented by a curve similar to the
ordinary binary freezing-point curve given by the two constituents in
question. Hence the observation of the $(n-1)$th freezing point
enables the ratio a of the remaining constituents to be estimated.

Any pair of constituents can be arranged to crystallise out last by
the addition of suitable amounts of certain of them, and thus by the
observation of the $(n-1)$th freezing points of $(n-1)$ solutions, the
composition of the original mixture of n substances is arrived at.

Binary mixtures $(n=2)$ are therefore analysed by one freezing-point
measurement. Ternary mixtures require two estimations of second
freezing points, quaternary mixtures three estimations of third freez-
ing points, and so on. The observation of third and higher freezing
points is very difficult, owing to the large amount of solid matter
already present. With ternary mixtures, it is necessary to obtain
two complete second freezing-point curves with mixtures of known
composition. Each of these curves represents the binary freezing-
point diagram of two constituents saturated with the third.

In some cases simplified methods are possible. For instance, when
the freezing-point diagram of a ternary mixture has the "ideal" form
the three binary curves are superposable. The influence of a quantity
of O on the solidifying point of P being the same as the influence of
an equimolecular quantity of M, is also the same as that of an
equivalent quantity of a mixture of O and M mixed. In this ideal
case the first freezing points of two solutions depositing P and O
respectively, say, are sufficient to establish the compositions of the
two solutions. This is tantamount to reducing a ternary mixture to
a binary one.

The method most used is to combine the two principles and establish

the composition of the solution by one first and one second freezing point measured successively. Similar simplifications are sometimes possible in the case of quaternary mixtures, particularly where some of the four constituents are isomeric substances.   R. J. C.

Relations of Isomorphism in Organometallic Compounds. III. Derivatives of Bivalent Metalloids. PAUL PASCAL (*Bull. Soc. chim.*, 1912, [iv], 11, 1030—1037. Compare A., 1912, i, 739).—The author has determined the freezing-point curves of binary mixtures of phenyl ether, phenyl sulphide, phenyl selenide, and phenyl telluride. These substances were each purified by fractional crystallisation, and were found to have the following melting points: $26°$, $-21·5°$, $2·5°$, and $4·2°$ respectively.

Phenyl sulphide and phenyl selenide give a continuous series of mixed crystals, the freezing-point curve passing through a minimum at $-26·7°$, corresponding with the mixture containing 5% of the selenide. Similar results are obtained with mixtures of the selenide and the telluride, the minimum point being $-4·2°$, corresponding with the mixture containing 80·4% of the selenide, and with mixtures of the sulphide and telluride, the mixture containing 83·42% of the sulphide having the minimum freezing point, $-30·7°$.

Phenyl ether and phenyl sulphide do not form a continuous series of mixed crystals, the freezing-point curve exhibiting a eutectic point at $-27·7°$, corresponding with a mixture containing 13·3% of the ether. The two series of mixed crystals in equilibrium at the eutectic point contain respectively 4·5 and 53% of phenyl ether.

The above results agree with the classification of sulphur, selenium, and tellurium, apart from oxygen.   T. S. P.

Internal Pressure and Latent Heat of Liquids. WILLIAM C. McC. LEWIS (*Phil. Mag.*, 1913, [vi], 25, 61—65. Compare A., 1912, ii, 136).—For the internal pressure of a liquid, the author has obtained previously the expression $K - l = TdK/dT$, where K is the internal pressure and l the latent heat of vaporisation of 1 c.c. According to Davies (A., 1912, ii, 902) the temperature-coefficient of the internal pressure dK/KdT is equal to the coefficient of expansion a, and by substituting in the above equation, it is found that $K = l/(1 + aT)$, which is identical with one of the results obtained by Davies.

If l is considered to represent the latent heat of expansion of the liquid (the heat absorption corresponding with isothermal expansion equal to 1 c.c.), it is deduced that $l = -Ta/\beta$. where a is the coefficient of thermal expansion and β the compressibility of the liquid. For non-associated liquids, the latent heat of expansion calculated from this equation is of the same order of magnitude as the latent heat of vaporisation. For associated liquids the differences are much greater.

Values representing the internal pressure are calculated for a number of liquids from the equation $K = l/(1 + aT)$ on the assumption that l is the latent heat of expansion. The numbers so obtained are approximately double those recorded previously.'   H. M. D.

Guldberg's Law and the Corresponding States. ANATOLE
LEDUC (*Compt. rend.*, 1913. **156**, 65—66).—A criticism of Boutaric's
deductions (this vol., ii, 21), in which the author suggests a modification
of Guldberg's law to read : the boiling points of substances under
equally reduced pressures are corresponding temperatures. W. G.

Composition and Pressure of the Vapour of Solutions.
M. S. VREVSKI (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1739—1747).—
The results previously obtained (A., 1912, ii, 1139) with aqueous
solutions of methyl, ethyl, and propyl alcohols containing from
20—30% to 100% of alcohol are in complete accord with the relation
established by Duhem and Margules between the partial pressures of
the vapours and the compositions of the solutions : $d \ln p_1/d \ln x =
d \ln p_2/d \ln(1-x)$. The applicability of this relation to the solutions
containing less than 20—30% of alcohol remains undecided, owing to
the lack of detailed experimental data.

The author discusses the numerical results, from which he draws the
following conclusions : (1) The displacement produced in the equi-
librium between solutions of two liquids and their saturated vapours,
with constant volume of the system, by change of temperature, is
subject to Le Chatelier and van't Hoff's law, which may he formulated
as follows : In all cases of equilibrium between phases of variable
composition, heating of the system under constant volume leads, in the
phase formed with absorption of heat, to increase of that component
the transformation of which absorbs the greatest quantity of heat.
(2) On the basis of Kirchhoff's theory, the change in the composition of
the vapour under the influence of temperature may be regarded as the
result of the combined action of two factors, the physico-mechanical
and the physico-chemical. In every system formed with either
development or absorption of heat, there exists a region of parallel,
and one of opposed, action of the two factors. The limits of these
regions are the solutions corresponding with the maximum or minimum
heat of formation. (3) The direction in which the change in composi-
tion of the vapour proceeds under the influence of temperature remains
the same for all concentrations of. the solution, if, in the region where
the actions of the two factors are opposed, the magnitude of the
physico-mechanical factor always predominates. (4) On change of
temperature of solutions formed without heat-effect, the variation in
the composition of the vapour takes place under the influence of a
single physico-mechanical factor and follows the same law as does
change in the composition of the vapour of mechanical mixtures ; (5)
with change of temperature of a solution which possesses a vapour-
pressure curve showing a maximum, the composition of the vapour and
that of the mixture with constant boiling point change in one and the
same direction. (6) If, however, the vapour-pressure curve shows
a minimum, the compositions of the vapour and that of the mixture
with constant boiling point change in opposite directions.
T. H. P.

**Association of Ethyl Ether and Chloroform in the Gaseous
State.** FRIEDRICH DOLEZALEK and ALFRED SCHULZE (*Ber. Deut. physikal.
Ges.*, 1912, **14**, 1091—1096).—It is shown that the mixing of the

vapours of ethyl ether and chloroform at 80° and atmospheric pressure is accompanied by contraction. When the volumes of the two vapours are equal, the data obtained correspond with a reduction of pressure of 4·8 mm. of mercury when the volume is kept constant. It is shown that the observed contraction is not due to deviations of the vapours from the gas laws, and the change in volume is consequently attributed to the formation of a compound. The magnitude of the volume change indicates that an equimolar mixture of ethyl ether and chloroform at 80° and atmospheric pressure contains 0·64 mol. % of the compound. By applying the law of mass action it is seen that the molecular proportion of the compound in the vapour mixture will increase almost in the same ratio as the total pressure. Similarly it is shown that the saturated vapour in equilibrium with an equimolar liquid mixture of the two substances at 80° should contain 1·4 mol. % of the compound. Since the liquid phase contains 14·6 mols. % of the compound it follows from the vapour pressure law for binary mixtures that the vapour pressure of the compound at 80° should be about 0·26 atmosphere.   H. M. D.

Isotherms of Diatomic Gases and of their Binary Mixtures. XI. Determinations with the Volumenometer of the Compressibility of Gases under Small Pressures and at Low Temperatures. W. J. DE HAAS (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 299—306. Compare A., 1912, ii, 1138).—The question of the distribution of pressure between the volumenometer and the piezometer used in the measurements of the compressibility of gases at low temperatures is discussed and a formula is deduced for calculating the change in the difference of pressure between the two communicating vessels as a function of the time. This formula involves the dimensions of the apparatus and the distribution of temperature along the connecting capillary. The curve corresponding with the formula is in satisfactory agreement with the actual observations of the change in the pressure difference with time.   H. M. D.

The Critical Point. ETTORE CARDOSO (*J. Chim. phys.*, 1912, 10, 470—496. Compare A., 1911, ii, 854).—In order to evaluate the compression coefficients of gases to 1 part in 10,000 for atomic-weight calculations, the critical temperatures and pressures must be known within the limits 0·1° and 0·1 atm. respectively. The temperature and pressure ought to be observed at the same time with the same specimen of gas, so that any error due to impurity may affect both values equally. Although various investigators have given critical pressures to within 0·01 atm., the author considers that they were not justified, since, in general, a variation of 0·001° in the temperature corresponds with 0·01 atm. in the pressure. At the same time it is admitted that observations of pressure or temperature made separately as by the Natterer tube may be more accurate than the author's as far as the actual specimen handled is concerned.

The paper describes the methods employed at Geneva in critical constant investigations. The gases were purified by fractional distillation under vacuum (compare Briner and Cardoso, A., 1909, ii,

124), alternating with passage through suitable absorbents maintained slightly above the boiling point of the gas. A sample of gas was not considered sufficiently purified until it could be liquefied at pressures constant to within 0·05 atm. at two different temperatures, one of which was near the critical point.

A manometer of the barometer type was used, consisting of a 1 mm. capillary tube with suitable bulbs in the upper and lower parts, surrounded with a glycerol-water jacket maintained at a constant temperature. It was filled with atmospheric nitrogen the compressibility of which is known from Amagat's accurate data. The manometer was read to 0·1 mm., corresponding with not more than 0·02 atm. pressure. Owing to the uncertainty of the capillary correction in a 1 mm. tube, closer reading would have been useless, and the use of a finer capillary would have introduced unknown errors due to diffraction and the retention of small gas bubbles below the meniscus. The different manometers agreed to within 0·1 atm. at least, and the accuracy of the methods was confirmed by the fact that concordant critical data were obtained with different manometers and different samples of gas, often at considerable intervals of time.

The working tube was provided with a small piece of soft iron wire constituting the armature of an electromagnetic agitator of the Kuenen type. On approaching the critical temperature, the meniscus disappears and the so-called "critical opalescence" is seen. The point of maximum opalescence is held by some to be the critical temperature (compare Nernst, "Theoretical Chemistry"). The opalescence usually extends over a range of 0·03°, but by means of the Kuenen agitator the range could be extended to 0·3° to 0·4°. The opalescence is therefore due to the formation of an emulsion of gas and liquid, which, being of nearly equal density, do not separate. The true critical point is taken as the point at which the opalescence disappears. This could be estimated to within ±0·05°, and is about 0·15° higher than the point of maximum opalescence. It is possible that an invisible opalescence persists at an even higher temperature, since in experiments made without the stirrer a slight diffraction could still be observed at the spot where the meniscus had been.

Critical data to the nearest 0·05 atm. and 0·05° are tabulated for hydrogen chloride, ammonia, carbon dioxide, sulphur dioxide, nitrous oxide, hydrogen sulphide, acetylene, ethylene, ethane, and cyanogen.

R. J. C.

Critical Constants of Ethane, Carbon Dioxide, and Sulphur Dioxide. ETTORE CARDOSO and R. BELL (*J. Chim. phys.*, 1912, 10, 497—503).—Ethane prepared from ethyl iodide by the Grignard reaction contained air and ethyl iodide and ether vapours as well as other impurities which were removed by suitable absorbents followed by fractional distillation. Ethane prepared by Frankland and Kolbe's method, by cautious addition of propionitrile to metallic sodium in a vacuum, was readily purified by absorbents only. The purified ethane, having m. p. −172·5°, and b. p., −84·1°, possessed an agreeable

ethereal odour. Its critical constants were $t_c = +32\cdot10^\circ \pm 0\cdot10^\circ$ and $p_c = 48\cdot85 \pm 0\cdot10$ atm.

Carbon dioxide, prepared by heating sodium hydrogen carbonate, was washed and fractionated ten times. Its critical constants were $t_c = +31\cdot00^\circ \pm 0\cdot10^\circ$ and $p_c = 72\cdot85 \pm 0\cdot10$ atm. The critical opalescence was observed as low as $30\cdot60^\circ$, but the point of maximum opalescence could not be decided.

Commercial sulphur dioxide was washed and purified by ten distillations. Its critical constants were $t_c = +157\cdot15^\circ \pm 0\cdot10^\circ$ and $p_c = 77\cdot65 \pm 0\cdot10$ atm. The point of maximum opalescence could not be observed owing to an opalescent deposit on the glass tube. This appeared to result from the action of light and heat on the sulphur dioxide, but it was ascertained that even 300 hours' heating did not alter the critical constants of the gas.   R. J. C.

Critical Constants of Ethylene, Nitrous Oxide, and Hydrogen Sulphide. ETTORE CARDOSO and E. ARNI (*J. Chim. phys.*, 1912, 10, 504—508).—Ethylene prepared by the action of sulphuric acid on ethyl alcohol and purified by washing and fractional distillation had m. p. $-169\cdot00^\circ$ and b. p. $-104\cdot3^\circ$. The critical constants were found to be $t_c = +9\cdot50^\circ \pm 0\cdot10^\circ$ and $p_c = 50\cdot65 \pm 0\cdot10$ atm. The critical opalescence extended from $+9\cdot05^\circ$ to $9\cdot50^\circ$.

Nitrous oxide was prepared by the action of saturated aqueous sodium nitrite on hydroxylamine hydrochloride in a vacuum. When washed and fractionated ten times it gave a perfectly colourless solid. The critical constants were $t_c = +36\cdot50^\circ \pm 0\cdot10^\circ$ and $p_c = 71\cdot65 \pm 0\cdot10$ atm. The critical opalescence extended from $36\cdot0^\circ$ to $36\cdot5^\circ$, and had its maximum at about $36\cdot3^\circ$.

Hydrogen sulphide prepared by the action of hydrochloric acid on purified precipitated iron sulphide in a vacuum was washed in water containing iron sulphide in suspension, and then dried and fractionated fourteen times in a vacuum. The purified gas of f. p. -83° and b. p. $-60\cdot2^\circ$ was without action on clean mercury, and was perfectly stable at the critical point. The critical constants were $t_c = +100\cdot40^\circ \pm 0\cdot10^\circ$ and $p_c = 89\cdot05 \pm 0\cdot10$ atm.   R. J. C.

Critical Constants of Ammonia. ETTORE CARDOSO and (Mlle.) A. GILTAY (*J. Chim. phys.*, 1912, 10, 514—516).—Ammonia was prepared by heating purified ammonium chloride with excess of calcined marble. It was dried by barium oxide and sodium wire, and distilled four times through the same reagents. Four further fractional distillations served to remove traces of air and hydrogen. The critical constants were $t_c = +132\cdot90^\circ \pm 0\cdot10^\circ$ and $p_c = 112\cdot30 \pm 0\cdot10$ atm.

The critical opalescence was observed from $132\cdot6^\circ$ to $132\cdot9^\circ$ with a maximum at about $132\cdot75^\circ$.   R. J. C.

Critical Constants of Hydrogen Chloride. ETTORE CARDOSO and A. F. O. GERMANN (*J. Chim. phys.*, 1912, 10, 517—519).—Purified sodium chloride was decomposed with pure concentrated sulphuric acid in a vacuum, the apparatus being constructed with fused joints throughout. The hydrogen chloride was dried with sulphuric

acid and phosphoric oxide, and fractionally distilled twelve times in all, first through phosphoric oxide and afterwards without it. The solidified hydrogen chloride was absolutely free from the pink tint usually attributed to a compound of phosphorus or to nitric oxide. It had m. p. $-111\cdot4°$, and h. p. $-83\cdot1°$. The critical constants were $t_c = +51\cdot40° \pm 0\cdot10°$ and $p_c = 81\cdot55 \pm 0\cdot15$ atm.   R. J. C.

Free Energy of Chemical Substances. Introduction. GILBERT N. LEWIS (*J. Amer. Chem. Soc.*, 1913, **35**, 1—30).—This paper is introductory to a series in which the free energy of chemical substances will be systematically studied. A detailed account is given of the general methods used in free energy calculations, including the consideration of the notation and fundamental units, the laws of energy, the change of energy with pressure, the relation between activity and fugacity and the free energy, free energy and the equilibrium constant, free energy and *E.M.F.*, and the influence of temperature on the free energy change.   E. G.

Tempering [of Metals] without Deformation. MAURICE HANRIOT (*Compt. rend.*, 1912, **155**, 1502—1504. Compare A., 1912, ii, 1137).—Cubes of a number of metals and alloys were submitted to high pressure when immersed in vaselin, and it was found that, whilst the cubes were not deformed and the internal structure, as examined micrographically for brass, was unaltered, the substances had undergone considerable tempering, as was shown by measuring their hardness, elongation, and breaking strain before and after the compression.

W. G.

The Rectilinear Diameter for Argon. ÉMILE MATHIAS, H. KAMERLINGH ONNES, and C. A. CROMMELIN (*Proc. K. Akad. Wetensch.*, 1912, **15**, 667—673).—A preliminary account is given of the apparatus and mode of procedure adopted in the determination of the densities of liquid and saturated vapour at a series of different temperatures. The mode of calculating the requisite data from the experimental observations is described, but no results are communicated.   H. M. D.

Specific Gravities of Saturated Aqueous Solutions of Various Salts at Different Temperatures. N. A. TSCHERNAJ (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1565—1576).—The author has determined the specific gravities (weights of 1 c.c.) of saturated solutions of a number of salts at intervals of $10°$ from $0°$ to $70°$ (or $90°$). These salts may be divided into two groups : (1) those forming saturated solutions which increase in specific gravity with rise of temperature and with increase in the salt content : potassium chloride, nitrate and sulphate, sodium and barium nitrates ; (2) those with which the reverse takes place : sodium chloride.

These salts also show different behaviour with reference to the variation with temperature of the quotient dP/dV, where dP represents the increase per $10°$ of the amount of salt (grams) dissolved by 100 grams of water, and dV the corresponding increase in volume (c.c.) of

the solution. With rise of temperature from $0°$ to $70°$, this quotient shows a contin·ous increase from 0.12 to 0.5 with sodium chloride, remains almost constant with potassium chloride (1.69), sodium nitrate (1.9), potassium nitrate (2.1), and potassium sulphate (2.2), and continually diminishes from about 5 to 1.6 with barium nitrate.

T. H. P.

Compressibility of Gases. GEORGES BAUME and E. WOURTZEL (*J. Chim. phys.*, 1912, 10, 520--522).—The relation of pressure to volume in sulphur dioxide, methyl ether, and chloroform vapour has been represented by the equation $pv = 1 + a(1 - L/L_1)$. where L is the density at pressure p, and L_1 the weight of a normal litre of the gas considered (compare Baume, A., 1908, ii, 372). The deviation coefficient a is numerically the same as Berthelot's deviation coefficient A^1_0 in the case of permanent gases, but with easily liquefiable gases $A^1_0 = a/(1 + a)$. This equation may be reduced to $A^1_0 = a - a^2$ when a^3 is negligible.

R. J. C.

Adsorption and Saturated Surfaces. ROBERT MARC (*Zeitsch. physikal. Chem.*, 1913, 81, 641—694 Compare Schmidt, A., 1910, ii, 1041; 1911, ii, 969).—The adsorption of a large number of substances on the crystal surfaces of barium sulphate, barium carbonate, rhombohedral calcium carbonate, strontium carbonate, lead carbonate, and lead sulphate was investigated by measuring the change in the refractive indices of the solution of many substances by means of an interferometer. It was shown that colloidal substances are easily adsorbed on crystal surfaces, whereas crystalline substances are only adsorbed to a very slight extent. Crystalline substances adsorb more if they are capable of forming isomorphous or mixed crystals with the adsorbing substances; thus potassium nitrate is adsorbed by barium carbonate, whilst sodium nitrate is not; on the other hand, sodium nitrate is adsorbed by rhombohedral calcium carbonate, whilst · potassium nitrate is not. The adsorption isothermals can be divided into three types : (1) Those in which a stronger bend is present than is demanded by the exponential formula, and which reach the saturation value continuously. (2) Those which agree at all points with the exponential formula. In this case, even though the measurements were made very close together, it was impossible to determine whether there was a break in the curve or not. (3) Those curves of substances which at low concentrations have a great tendency to be adsorbed, and give a very steep curve and reach the saturation point at very low concentrations. The adsorbed substance is the factor which conditions the type of curve in any case. It is shown that when the saturation values for a series of substances with one given adsorbing medium have a given ratio, then the ratio of the saturation values for those substances with another adsorbing medium will be the same. The formulæ of Schmidt and Arrhenius are discussed, and it is shown that the Arrhenius formula holds well for substances giving curves of the first type, but for curves of the second type it holds only over a portion of the curve and ceases to hold some distance before the saturation value is reached, whilst for curves of the third type it

does not hold at all. It is, however, shown that the Arrhenius formula probably represents ideal conditions which are only existent when molecular compounds are not formed in the adsorption layer.   J. F. S.

Adsorption. VII. Chemical Hysteresis of Starches. Adam V. Rakovski (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1722—1728).— The investigations here described are a continuation of those published in papers I. and II. (A., 1911, ii, 470), and deal with curves intermediate to those of hydration and dehydration of Bermuda arrowroot and rice starches. These intermediate curves are found to be virtually reversible, but not throughout their whole length. Detailed study of such curves would, however, be possible only with colloids showing a considerably greater separation of the curves of hydration and dehydration than is the case with starches.

The presence of about 1% of mercuric chloride in potato starch exerts no appreciable influence on the course of either hydration or dehydration.   T. H. P.

Relation between the Conductivity of Acids and their Absorption by Hide. André Brochet (*Compt. rend.*, 1912, **155**, 1614—1617).—Measurements have been made of the amount of acid absorbed by shaking 10 grams of hide powder for four hours with 200 c.c. of an $N/10$-solution of the acid concerned, containing 100 grams of sodium chloride per litre. Measurements have been made with three classes of acids varying in conductivity, namely : (1) good conductors, (2) moderate conductors, (3) poor conductors. In class (1) inorganic acids and organic acids of the type of trichloroacetic acid were examined. The absorption of acids by the hide is a general phenomenon, and is the result of a chemical combination, the amount of acid absorbed being proportional to the chemical equivalent of the acid. The fraction of the gram-equivalent of acid absorbed by one kilo. of dry hide, whilst constant for each class, does show a slight diminution with diminution in conductivity ; but while the absorption diminishes only in the ratio 3 : 2, the conductivity diminishes as 100 : 1.   W. G.

Some Properties of the Thiocyanate Ion. Herbert Freundlich and A. N. Seal (*Zeitsch. Chem. Ind. Kolloide*, 1912, **11**, 257—263).—The lyotropic properties of solutions of potassium chloride and potassium thiocyanate have been compared in a quantitative manner with the object of determining the position of the thiocyanate ion in the lyotropic series. The properties examined were the following : the influence of the electrolyte on the solubility of benzoic acid, the effect on the surface tension, the absorbability by animal charcoal, the retarding influence on the rate of ester saponification, and the effect on the rate of increase of the viscosity of gelatin solutions. The observations show that the lyotropic influence of the thiocyanate ion is distinctly smaller than that of the chloride ion, and that its position in the series of anions is close to the iodide end in the

series : fluoride, sulphate, phosphate, chloride, nitrate, bromide, iodide. In this series the lyotropic influence diminishes from left to right.

<div align="right">H. M. D.</div>

Surface Tension of Protein Solutions. II. FILIPPO BOTTAZZI and E. D'AGOSTINO (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 561—572. Compare Bottazzi, A., 1912, ii, 1042).—The paper records in tables and curves the results of further experiments with Traube's stalagmometer on solutions of serum-albumin to which various quantities of hydrochloric acid, sodium hydroxide, or sodium chloride were added. From the experiments it appears that the value n (number of drops) depends entirely on the undissociated molecules of the protein or of its salts, for an increase in the concentration of these molecules increases n (that is, the surface tension is lowered). In order to obtain the maximum dissociation of the albuminate, it is necessary to add more acid or alkali in weak solutions than in stronger ones. This indicates the presence of salts of a weak base (or acid), and for the same reason the maximum dissociation will be reached only when more than the equivalent amount of sodium hydroxide or of hydrochloric acid is added. From the amounts thus added it appears that the molecular weight of the albumin should be somewhat above 1000. From the curves it also appears that the albumin chloride is much less dissociated than the sodium albuminate at the same dilution. The addition of sodium chloride diminishes the dissociation of both the albumin salts, but its influence is much greater on the chloride than on the albuminate. The addition of sodium chloride also diminishes the dissociation of the free albumin, probably owing to the formation of undissociated secondary products.   R. V. S.

Molecular Complexity in the Liquid State. WILLIAM E. S. TURNER (*J. Chim. phys.*, 1912, 10, 467—469. Compare Guye, A., 1911, ii, 1067).—The author agrees with Guye that liquids which give a high value of Ramsay and Shields' constant are not necessarily dissociated, since error may arise from abnormality in the surface film of the liquid, but cannot agree that in his experiments, criticised by Guye, the surface films of diphenylamine and phenylurethane were oxidised. The value obtained with diphenylamine was in accord with that obtained by Dutoit and Friedrich (A., 1900, ii, 194).   R. J. C.

Mode of Ionisation of Sulphuric Acid in Dilute Aqueous Solutions. JOSEPH A. MULLER (*Compt. rend.*, 1912, 155, 1499—1502). —From a series of determinations of the coefficients of ionisation and heat of dilution of aqueous solutions of sulphuric acid, the author deduces that, in dilute aqueous solutions, sulphuric acid is ionised into the two ions SO_4H' and H', and that this ionisation is accompanied by development of heat within the limits of the experimental temperatures (14—38°).   W. G.

Application of the Theory of Chemical Potential to the Thermodynamical Theory of Solutions. III. Action of Gravity on a Solution. The Solute Potential. Extension of the Theory. SYDNEY A. SHORTER (*Phil. Mag.*, 1913, [vi], 25, 31—42. Compare A., 1912, ii, 24, 437).—From a general theorem

ennnciated by Gibbs, the author deduces a formula for the influence of gravity on a binary mixture. This formula is found to be in accordance with the equation obtained directly by Duhem. Formulæ are also given for the practical calculation of the gravity effect from osmotic pressure, vapour pressure, and freezing-point data.

In the second part of the paper, the theory given in Parts I and II, (*loc. cit.*) is extended to solutions containing any number of non-volatile solutes. Exact formulæ are deduced connecting the osmotic pressure, vapour pressure, and freezing point with the lowering effect exerted by the solutes on the chemical potential of the solvent. Thermo-dynamically, the solutes may be regarded as a single substance, and hence the formulæ relating to a binary solution may be generalised in a very simple manner.   H. M. D.

Studies of the Processes Operative in Solutions. XX. The Conversion of Ammonium Cyanate into Carbamide, Especially as Influenced by Alcohols. ERIC E. WALKER (*Proc. Roy. Soc.*, 1912, *A*, 87, 539—554. Compare J. Walker and Kay, T., 1897, 489).—Experiments have been made to determine the influence of ethyl, propyl, and *iso*butyl alcohol on the rate of trans-formation of ammonium cyanate into carbamide when the ratio of cyanate to water in the solution is kept constant. The measurements were made at 40°, and the rate of change at any moment was obtained by determining the tangent to the smooth curve drawn through the points representing the cyanate concentrations after a series of time intervals.

In aqueous solution the rate of change varies approximately as the square of the concentration of the cyanate, as found by Walker and Hambly (T., 1895, 71, 746), but the carbamide and ammonium carbonate which are formed have some influence on the velocity. Since the carbonate is formed very rapidly at the beginning of the experiment, the velocity coefficient is abnormally high at first, and during the later stages of the change the coefficient is again too large because of the accelerating effect of the ammonium carbonate. The addition of carbamide to the original solution has also the effect of increasing the mean velocity coefficient, a result which is probably due to its influence on the side-reaction by which ammonium carbonate is produced.

The data obtained in a series of experiments in which the molar ratio of ammonium cyanate to water was 0·15 : 100, and in which the number of mols. of ethyl alcohol was increased from 0 to 120 per 100 of water, show that the rate of change is increased in proportion to the amount of alcohol present. When the alcohol and water are present in equimolar proportions, the rate of change is, however, only about five times as large as the rate in the absence of alcohol (compare Walker and Kay, *loc. cit.*).

From comparative experiments in which ethyl, propyl, and *iso*butyl alcohols were added to the aqueous solution of the cyanate, it appears that the activity increases considerably with the molecular weight of the alcohol. The percentage increase in velocity per mol. of added alcohol was found to be 3·30%, 4·92%, and 7·3% respectively for a solu-

tion containing 0·15 mol. of cyanate per 100 mols. of water. The order in which the alcohols are arranged is the same as that obtained on contrasting their activities as precipitants of salts from aqueous solutions and their physiological activity as hormones. It is supposed that the action of the alcohols is largely mechanical, the larger molecules having the greater effect both on account of their size and their greater mobility by reason of their smaller affinity for water.

H. M. D.

Studies of the Processes Operative in Solutions. XXI. Hydrolysis of Sucrose by Dilute Acids. FREDERICK P. WORLEY (*Proc. Roy. Soc.*, 1912, *A*, 87, 535—563).—The conclusion drawn by Armstrong and Caldwell (A., 1904, i, 1070), that the hydrolytic action of dilute acids on sucrose is closely analogous to that of enzymes, has been subjected to examination in a further series of experiments with dilute sulphuric acid at 25°. In three comparative observations the solutions contained 0·01 mol. acid, 200 mols. of water, and 1, 2 and 4 mols. of sucrose respectively. From the measured time changes in the rotation of the solutions, it is evident, that the rate of hydrolysis diminishes as the reaction proceeds in accordance with the requirements of the mass law. The view that the hydrolysis in dilute acid solution is characterised by an initial period in which the sucrose is hydrolysed at a constant rate, finds no support from the data which have now been obtained. There is, therefore, a considerable difference between the sucroclastic action of dilute acids and small quantities of enzymes.

It is pointed out that this conclusion has already been drawn by Rosanoff, Clark and Sibley (A., 1912, ii, 34), but that the arguments put forward by these authors are unsound.   H. M. D.

Studies of the Processes Operative in Solutions. XXII. Hydrolysis of Sucrose by Sulphuric Acid; Improvements in Polarimetric Apparatus. FREDERICK P. WORLEY (*Proc. Roy. Soc.*, 1912, *A*, 87, 563—581).—Similar experiments to those described in previous papers have been made with sulphuric acid as a catalyst in order to ascertain the influence of dilution on the hydrolytic activity in the case of a dibasic acid. The various substances were used in the proportion of 1 mol. of sulphuric acid, 30 to 200 mols. of water, and either 0·125 or 0·25 mol. of sucrose. From the velocity coefficients at the different dilutions, the value of the apparent molecular hydration has been calculated. This increases from 12·2 to 15·8 when the molar ratio of water to acid increases from 30 to 80, remaining practically constant on further dilution. By comparing the results with those obtained for hydrochloric, nitric, and *p*-dichloro- and *p*-di-iodobenzenesulphonic acids, it is found that the maximum apparent hydration is reached at an earlier stage in the case of sulphuric acid than when the monobasic acids are employed as catalysts.

From the final and initial rotations of the differently concentrated solutions it appears that the degree of optical inversion varies with the dilution. In the case of the most concentrated solution, the ratio of the rotations was found to be 0·342, whereas 0·298 was obtained for the most dilute solution. This variation is attributed to the influence

of the acid on the rotatory power of the sugars present, the lævulose being responsible in all probability for the major part of the effect. In view of this phenomenon and of the influence of the mutarotation of the dextrose and lævulose, it might be doubted whether the polarimetric method affords a satisfactory measure of the rate of hydrolysis of sucrose.   A theoretical examination of the subject from this point of view shows, however, that the velocity coefficient is not affected either by an alteration in the rotatory power of the invert sugar as a consequence of the presence of the acid or by the muta-rotation of the monoses.

Considerable improvements have been made in the apparatus employed for the polarimetric study of chemical changes, and these, together with the precautions which must be observed in accurate work, are described in detail.   H. M. D.

Studies of the Processes Operative in Solutions. XXIII. Hydrolysis of Methyl Acetate by Acids. FREDERICK P. WORLEY (*Proc. Roy. Soc.*, 1912, *A*, 87, 582—603. Compare Armstrong and Watson, A., 1907, ii, 849).—With the object of determining the apparent molecular hydration of the acid by the method employed in connexion with the hydrolysis of sucrose (P., 1910, 26, 298), measurements have been made of the rate of hydrolysis of methyl acetate under the influence of hydrochloric acid. The experiments were carried out at 25°, the molecular proportions of the substances employed being 1 of methyl acetate, 120 of water, and from 0·6 to 4 of hydrochloric acid.

Under these conditions, the proportion of methyl acetate ultimately hydrolysed is never greater than 95%, and in consequence it is necessary to take the reverse change into account in calculating the velocity coefficient of the hydrolysis, the reaction taking place in accordance with the equation $dx/dt = k(a-x) - k^1x^2$, in which a is the initial concentration of the ester, and x the amount transformed after time t.

For a given ratio of water and methyl acetate, the proportion of the latter which is hydrolysed when equilibrium is attained decreases slightly as the concentration of the catalyst increases.   In view of this it is suggested that the usual interpretation of the equation

$$k[CH_3 \cdot CO_2CH_3][H_2O] = k^1[CH_3 \cdot CO_2H][CH_3OH]$$
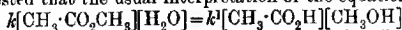
is incorrect, and that since hydrolysis is probably effected by the direct interaction of hydrated hydrolyte and hydrated catalyst, the factor $[H_2O]$ does not necessarily represent the active mass of one of the substances taking part in the reaction, but probably expresses the degree of dilution.

From the velocity coefficients, values representing the apparent molecular hydration of the hydrochloric acid have been obtained. Corresponding values have also been calculated for sodium, potassium and ammonium chlorides from the increase which these salts produce in the velocity coefficient. These molecular hydration values are much smaller than the corresponding numbers obtained when sucrose and raffinose are used as hydrolytes. Whereas with methyl acetate the apparent hydration value increases from 2·5 to 5 when the molecular

ratio of water to acid increases from 30 to 80, the corresponding series of numbers from the data for the hydrolysis of sucrose increases from 13 4 to 18·7. It is considered probable that the differences involved represent actual differences in the condition of the acid in presence of such different hydrolytes as methyl acetate and sucrose.   H. M. D.

Studies of the Processes Operative in Solutions. XXIV. Nature of the Hydrolytic Process. HENRY E. ARMSTRONG and FREDERICK P. WORLEY (*Proc. Roy. Soc.*, 1912, A, 87. 604—623).— The authors discuss the general character of the results obtained in this series of papers and their theoretical interpretation. As indicated in previous communications, the view is put forward that hydrolysis is essentially an associative process which involves the association and direct interaction of two complexes, one of which consists of the hydrated hydrolyte and the other of the hydrated catalyst. Such associated systems are being constantly produced, broken down and reformed in such a manner that while some give rise to the original components, others are resolved into the products of change. According to this view, hydrolysis is a bimolecular change, the second factor being the active mass of the hydrated catalyst, and not, as is generally supposed, the active mass or concentration of the water. The similarity of the results arrived at by the study of different properties, such as electrical conductivity, hydrolytic activity and osmotic effects, is quite consistent with this view, the similarity being due to the fact that the determining factor in all these cases is the interaction involved in the production of the electrolyte from water and the solute.

The increase of molecular conductivity to a maximum on dilution is attributed partly to a gradual increase in the extent of the interaction between the solute and water, and partly to the gradual simplification of the complexes formed by the dissolved substance. On the other hand, the decrease of electrical activity, as exemplified by the hydrolytic activity of the acids, to a minimum on dilution is considered to be the necessary result of a gradual weakening of the acid by further combination with water. The greater the extent to which the activity of the acid is used up in combining with water, the less must be the residual activity available for hydrolytic processes.

Stress is laid on the fact that this associative theory is directly opposed to the generally accepted dissociative hypothesis, and it is claimed that the facts disclosed in the investigation of the processes operative in solution go far to show that this hypothesis is no longer tenable.   H. M. D.

Intercrystalline Cohesion in Metals and the Formation of Twinned Crystals in Silver. WALTER ROSENHAIN and DONALD EWEN (*J. Inst. Metals*, 1912, 8, 149—185).—Many of the properties of metals, especially at high temperatures, may be accounted for by assuming the presence of an amorphous film between the crystals. The hypothesis has been tested in the following manner. The amorphous modification, being unstable, should have a higher vapour-

pressure than the crystalline. Two specimens of silver are taken, one having coarse and the other fine crystals. The latter, which has a larger area of intercrystalline boundaries in unit volume than the former, always loses weight more rapidly when heated in a vacuum. Similar results are obtained with zinc and copper. Microscopical examination shows that the intercrystalline boundaries are developed, as if by etching, by such treatment. Boundaries between twin crystals are not thus affected.

Cast silver, even without any mechanical treatment, shows numerous twinned crystals, which are revealed by heating in a vacuum.

C. H. D.

⌐·Formation of Twin Crystals by Quenching and its Influence on the Hardness of Metals. CHARLES A. EDWARDS (Internat. Zeitsch. Metallographie, 1912, 3, 179—194).—The light and dark acicular structure observed iu quenched alloys of copper and aluminium, containing 9—16% Al, is not due to the presence of two constituents, but to repeated twinning, brought about by the mechanical pressure due to quenching. The vitreous modification of the metal is formed at the surfaces of slip, thus increasing the hardness of the alloys. This explanation is extended to the general case of hardening of alloys by quenching.   C. H. D.

Etching at High Temperatures. H. HANNEMANN (Internat. Zeitsch. Metallographie, 1912, 3, 176—178).—The method of investigating the crystalline structure of alloys at a high temperature by exposure to etching vapours is faulty, because the surface etched is not a section through a crystal, but the surface of a crystal, and segregation is not thereby revealed. Further, recrystallisation may take place during the action of the reagent, thus producing a false structure.   C. H. D.

Colloids. PAUL BARY (J. Chim. phys., 1912, 10, 437—453. Compare A., 1911, ii, 702).—Colloidal solutions comprise three classes, namely : (1) Jellies, which are solutions of liquids in solids of great cohesive power. (2) Electrical colloids, which are suspensions of very fine insoluble powders without solvent power, which acquire au electrical charge. in contact with the liquid. Colloids of this class exhibit Brownian motions, and are coagulated by reducing their electrostatic charges. (3) Mixed colloids consisting of micella formed from irregular particles of jelly by the action of excess of liquid. These micella exhibit Brownian motions and may acquire an electrostatic charge. They can therefore be coagulated by altering the external osmotic conditions or by electrical methods, or by both combined according to circumstances.

The micella in class (3) are to be regarded as minute osmotic cells into which the surrounding liquid diffuses until its pressure is balanced by the surface tension or cohesion of the small particles. The surface tension of the colloidal substance is negative to start with and tends to approach zero as the jelly becomes saturated. Caoutchouc (Red Tonkin, unvulcanised) absorbs approximately the same volumes

of chloroform, benzene, carbon disulphide, and tetrachloroethane to form saturated jellies before breaking up into micella.

In some cases the surface tension does not attain zero, so that the limit of osmosis inwards is reached in the jelly stage, and the true solution of class (1) does not pass into a pseudo-solution of class (3) on further addition of liquid. Examples of this are the swelling of gelatin in cold water and of cellulose tetra-acetate in cold tetra-chloroethane. In such cases micella can usually be obtained from the jellies by heating or even by violent agitation. The jelly separates out again on cooling, as with cellulose tetra-acetate, unless Brownian motion and electrification of the micella supervene as in the case of gelatin.

R. J. C.

Determinations of the Volume of Voids in Silicic Acid Gels. WILHELM BACHMANN (*Zeitsch. anorg. Chem.*, 1912, 79, 202—208).— The transient opacity of silica gels during dehydration has been considered by Tschermak and also by Tammann to indicate the appearance of a new hydrated phase. On the other hand, the fact that the same change is observed when such different liquids as cedar oil or a mixture of olive oil and chloroform are used, indicates that the process is one of mechanical imbibition. The view of Zsigmondy (A., 1911, ii, 880 ; Bachmann, A., 1912, ii, 145) that the gel is traversed by minute capillaries accords best with the facts. It is now shown that the weight of different liquids taken up by a gel is proportional to their density. The gel is prepared by exposing glassy silicic acid to steam, and then washing with water and drying over sulphuric acid. Three gels are examined, the liquid being generally introduced by exposure to its vapour.

Measurements with water, benzene, chloroform, ethyl iodide, and acetylene tetrabromide, the last being used in the liquid form only, give concordant results.

C. H. D.

Theory of Emulsification. IV. WILDER D. BANCROFT (*J. Physical Chem.*, 1912, 16, 739—758. Compare A., 1912, ii, 834). —Robertson's paper on emulsions of oil and water (A., 1910, ii, 697) and the article on emulsions in Remington's "Practice of Pharmacy" (1907) are reproduced in full.

Robertson's work is valuable because he was able to prepare emulsions of water in oil as well as of oil in water. Moreover, by means of an especially efficient shaker, he emulsified the whole of his ingredients in one operation instead of working in the dispersed phase gradually. The author holds that this successful preparation of emulsions of water in oil was due to the fact that the olive oil used has some solvent power for the emulsifier, sodium oleate, whereas kerosene and benzene, in which the soap is insoluble, give no such emulsions. The author does not accept the conclusion drawn by Robertson that one type of emulsion passes into the other at a definite concentration, but argues that there may be a range of concentrations within which no emulsion whatever is produced, or the emulsions may overlap.

The emulsions known to Pharmacy, which contain upwards of 95% of oil, are all of the oil in water type with gum acacia, egg-albumin, or

casein as emulsifying agents. The object of the pharmacist is to divide the oil into minute globules, and surround each one with an adhesive envelope. The exact proportions of oil, water, and gum are probably not so important as is generally supposed.   R. J. C.

Composition of the Disperse Phase in Emulsoids. EMIL HATSCHEK (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 284—286).—On the assumption that the velocity of displacement of the juxtaposed layers exceeds a certain critical value, it has been shown (A., 1911, ii, 98) that the viscosity, η', of an emulsoid is given by the equation $\eta' = \eta \sqrt[3]{A}/(\sqrt[3]{A} - 1)$, in which η is the viscosity of the dispersive medium and A is the ratio of the volume of the emulsoid to that of the disperse phase. If the viscosity of the pure dispersive medium is taken as unity, this equation gives $A = \{\eta'/(\eta' - 1)\}^3$. From the viscosity data for a series of glycogen and sodium casein hydrosols, the author has calculated the values of A given by this formula. When these values are compared with the values of A', representing the ratio of the volume of the emulsoid to the weight of disperse phase present, it is found that the ratio of A' to A remains very nearly constant if the less concentrated hydrosols are left out of account. The constancy of this ratio indicates that the disperse phase consists, at a given temperature, of the dissolved substance together with a definite and constant quantity of the dispersive medium.   H. M. D.

The Existence and Probable Thickness of Adsorption Envelopes on Suspensoid Particles. EMIL HATSCHEK (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 280—284).—The properties of suspensoid systems which depend on the movements of the particles indicate that the volume of the disperse phase is not independent of the degree of dispersity. On the assumption that this is due to the formation of an envelope of the dispersive medium round each suspensoid particle, and that the thickness of the covering film is constant for varying degrees of dispersity, it can be shown that the effective volume, V', and the actual volume, V, of the disperse phase are connected with one another by the equation $V'/V = (1 + 3t/r)$, where r is the radius of the nucleus of disperse phase and t is the thickness of the envelope of dispersive medium. From this, it is evident that the effective volume of the disperse phase will increase continuously as the degree of dispersity increases.

Experimental measurements have shown that the viscosity of highly disperse systems increases with the degree of dispersity when the proportion of disperse phase is kept constant, and this is probably due to the increasing importance of the surrounding envelope of dispersive medium.

From Odén's measurements of the viscosity of colloidal sulphur solutions of different degrees of dispersity (A., 1911, ii, 971 ; 1912, ii, 240), the author has calculated, by means of the above formula, the thickness of the surrounding envelope to be $0.87\mu\mu$. Accepting this value, it follows that, for colloidal particles of diameter $10\mu\mu$, the volume of the envelope amounts to 62% of the volume of the colloidal sulphur.   H. M. D.

The Equilibrium of a Gas in a State of Binary Dissociation. J. DE BOISSOUDY (*Compt. rend.*, 1913, 156, 61—64).—A mathematical discussion of the equilibrium of a gas such as nitrogen peroxide, acetic acid vapour, etc., when partly dissociated into two identical constituents. The equilibrium is expressed by the equation

$$x^2/v(1-x) = MT^2 e^{-\frac{x}{\hat{v}T}}$$

where x is the degree of dissociation, v the volume containing one gram-molecule, T the temperature, χ the energy necessary to dissociate the normal molecules into their constituents, and M a constant coefficient. W. G.

Action of Temperature on the Equilibrium of Nitrous and Nitric Acids Formed from the Oxides of Nitrogen and Water. EMIL BRINER and E. L. DURAND (*Compt. rend.*, 1912, 155, 1495—1497).—In a previous paper (A., 1912, ii, 1045) the authors studied the effect of pressure and concentration on various systems of oxides of nitrogen and water, the temperature remaining constant. They have now estimated the relative molecular amounts of nitrous and nitric acids formed in the solutions at varying temperatures, and find that increase in pressure of the nitric oxide and diminution of temperature favour the formation of nitrous acid. W. G.

The Equilibrium in Acid Solutions of Potassium Salts. II. ALBERT J. J. VANDEVELDE (*Bull. Soc. chim. Belg.*, 1912, 26, 513—532. Compare A., 1912, ii, 30).—A continuation of the study of the constitution of the solid phase obtained from acid solutions of potassium salts. In the former communication the salt chosen was potassium sulphate and the three acids, hydrochloric, nitric and sulphuric. To complete this study the equilibrium has been determined (1) for solutions of potassium chloride, (2) for solutions of potassium nitrate, mixed in turn with one of the three above-mentioned acids in such proportions as to produce a solid phase. In the systems studied the same results are obtained by having present the same ions in equal quantities, independently of the manner of their original combination ; thus from solutions containing $20KCl : 10H_2SO_4$ or $10K_2SO_4 : 20HCl$, the solid phase in each case had the composition $8KCl : 4KHSO_4$.

In the system potassium chloride, sulphuric acid, and water, the solid portion was only a single phase, consisting of potassium chloride when the sulphuric acid was in the proportion $40KCl : 5H_2SO_4$ or less, the solubility of the chloride diminishing as the concentration of the acid diminished. On replacing the sulphuric acid in the system by hydrochloric acid, the solid phase was always potassium chloride, the solubility increasing with diminution in concentration of the acid. In the system potassium chloride, nitric acid, water, the solid phase in all cases contained both potassium chloride and nitrate, the amount of the former diminishing and of the latter increasing with rise in concentration of the acid.

In the case of potassium nitrate, sulphuric acid, and water, the

solid phase consisted solely of potassium nitrate, and its solubility seemed but very slightly affected by the concentration of the acid.

On replacing the sulphuric acid with nitric acid, the nitrate was found to be less soluble, but to an extent independent of the acid concentration. In the system potassium nitrate, hydrochloric acid, water, the solid portion was a single phase, potassium nitrate, until the acid reached the concentration $20KNO_3 : 20HCl$.   W. G.

Heterogeneous Equilibria between Aqueous and Metallic Solutions. II. Interaction of Mixed Salt Solutions and Liquid Amalgams. GEORGE MCPHAIL SMITH (*J. Amer. Chem. Soc.*, 1913, **35**, 39—49. Compare A., 1910, ii, 401).—This work was undertaken for the purpose of studying by an independent method the ionisation relations existing in mixtures of salts. By agitating dilute sodium or potassium amalgam with successive portions of a solution of sodium and potassium chlorides or sulphates, a mixture is soon obtained in which at equilibrium the concentrations of the salts in the mixed solution are identical with those in the original salt solution; the amalgams are then analysed.

The ion fractions of sodium and potassium in experiments in which the salts were present in equivalent quantities have been calculated on the assumptions that (1) the reaction takes place according to the equation $KHg_m + Na^{\cdot} \rightleftarrows NaHg_n + K^{\cdot} + (m-n)Hg$, and (2) that in the solutions containing a common ion and having a total salt concentration $0\cdot2N$, the relation Na salt/K salt $= Na^{\cdot}/K^{\cdot}$ is approximately true. The results show that the sodium ion fraction increases with the total salt concentration of a solution. In order to explain this phenomenon, it is suggested that sodium and potassium chlorides in mixed aqueous solution form the complexes $Na(Cl\cdot K\cdot Cl)$ and $K(Cl\cdot Na\cdot Cl)$. The formation of the latter complex would lower the value of the sodium ion fraction, and the conclusion is therefore drawn that the preponderating complex is $Na(Cl\cdot K\cdot Cl)$, and that this ionises into $Na^{\cdot}$ and $(Cl\cdot K\cdot Cl)'$ ions.   E. G.

Influence of Temperature on the Velocity of Chemical Reactions. I. B. SCHVECOV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, *Phys. Part*, 470—474).—Owing to the inconstancy of the ordinary temperature-coefficient of chemical reactions which is represented by the expression $\gamma = (K_2/K_1)10/(t_2 - t_1)$, where K_1 and K_2 are the velocity constants at the temperatures t_1° and t_2° respectively, Plotnikov (A., 1905, ii, 376) suggested the use of the so-called logarithmic temperature-constant given by $a = (\log K_2 - \log K_1)/(t_2 - t_1)$. Comparison of these two equations shows that a would be constant only over intervals of temperature for which γ gives constant values. Auerbach (A., 1905, ii, 571) has, indeed, shown that Plotnikov's logarithmic temperature-constant is a variable magnitude.

From theoretical considerations, the author regards it as more likely that constant values will be obtained for the ratio between the velocities of reaction if these are calculated for absolute temperatures having a constant ratio (ρ). The logarithmic temperature-coefficient, η, would then be given by the equations: $\eta = K\rho T/KT$, $\eta = K\rho^2 T/K\rho T$,

. . . . . , $\eta = K\rho^n T / K\rho^{n-1} T$. The product of all these equations gives $\eta^n = K\rho^n T / KT$, or, if $K\rho^n T = K_2$, $KT = K_1$, $\rho^n T = T_2$ and $T = T_1$, $\rho^n = T_2/T_1$ or $n = (\log T_2 - \log T_1)/\log \rho$. Hence,

$$\eta = \sqrt[n]{K\rho^n T / KT} = (K_2/K_1) \log \rho / \log T_2 - \log T_1.$$

The relation between this logarithmic coefficient η and the ordinary cofficient γ is expressed by the equation :

$$\log \eta = \frac{\log \rho}{10} \cdot \frac{T_2 - T_1}{\log T_2 - \log T_1} \cdot \log \gamma.$$

Taking ρ to be 1·1, that is, an increase of 10% in the absolute temperature, the values $\gamma_1 = 2$ and $\gamma_2 = 3$ for the ordinary coefficient at ordinary temperatures give $\eta_1 = 7·23$ and $\eta_2 = 23·02$ respectively. On the assumption that the latter magnitudes remain constant, the corresponding values for γ at different absolute temperatures will be as follows :

$T.$	$\eta_1, 7·23.$	$\eta_2, 23·02.$
100	$\gamma_1 = 8·00$	$\gamma_2 = 27·02$
150	3·98	8·93
200	2·84	5·22
300	2·00	3·00
1000	1·23	1·38

These numbers are in agreement with the general variation of the ordinary temperature-coefficient, which diminishes with rise, and rapidly increases with fall, of the temperature. In the particular case of the decomposition of hydrogen iodide, the values of γ calculated by means of the above equation agree, within the limits of experimental error, with the observed values ; thus for the temperature-intervals 300—400°, 400—500°, and 500—600°, Bodenstein (A., 1899, ii, 637) found 1·89, 1·64, and 1·53 respectively, the calculated values being 1·94, 1·64, and 1·49.   T. H. P.

The Relation between Oxidation Potential and Oxidation Velocity JULIUS GRÓH (*Zeitsch. physikal. Chem.*, 1913, 81, 695—712. Compare Bodenstein, A., 1904, ii, 717 ; Bognar, A., 1910, ii, 282).— The oxidation of acetaldehyde and formic acid was effected by means of chlorine, and the velocity constants determined. Considerable difficulty was experienced owing to the reactions being complicated through the action of the chlorine on water; however, by effecting the changes in the presence of a known concentration of nitric acid, it became possible to bring the secondary reaction into the calculation, and obtain a moderately good velocity constant.

Other experiments, namely, the action of iodine on acetaldehyde, the oxidation of aldehyde by cerium ammonium nitrate, and the oxidation of chloral and bromal with bromine were tried, but were found to be too complicated to furnish results. The velocity of oxidation by chlorine in the two cases investigated when compared with Bognar's results for bromine (*loc. cit.*) show that they are just opposite to the oxidation potentials of chlorine and bromine, thus :

|	Acetaldehyde.		Formic acid.	
	Br.	Cl.	Br.	Cl.
Velocity constants	1·205	0·648	3280	431
Oxidation potential ...	1·334	1·639	1·334	1·639

This anomaly can be explained in two ways: (1) The chemical resistance is greater in the case of chlorine than in that of bromine. (2) That the course of the reaction is different in the two cases. The first reason is held by the author to be unlikely, the second case becomes likely if it is supposed that the halogen forms an intermediate compound with the reducing substance, which breaks up with greater or lesser velocity to form the end products of the reaction. Attempts were made by spectrophotometric measurements to confirm the second conclusion, but they led to no definite results.   J. F. S.

Velocity of Reaction of Different Bases with Halogen-substituted Acids. II. HJ. JOHANSSON (*Zeitsch. physikal. Chem.*, 1913, 81, 573—589. Compare A., 1912, ii, 544; Holmberg, A., 1912, ii, 443; Senter, T., 1912, 91, 460).—The velocity of reaction of the decomposition of monobromosuccinic acid is investigated in neutral and alkaline solution and also in the presence of neutral salts. It is shown that two reactions take place, the first unimolecular, in which the hydroxyl ion reacts with the ion of monobromosuccinic acid with the production of the ion of fumaric acid and bromine ion, thus:

$$'O \cdot CO \cdot CHBr \cdot CH_2 \cdot CO \cdot O' + OH' = 'O \cdot CO \cdot CH:CH \cdot CO \cdot O' + Br' + H_2O,$$

and the second, a bimolecular reaction in which the ion of monobromosuccinic acid forms first the ion of propiolactonecarboxylic acid and bromine ion, thus:

$$'O \cdot CO \cdot CHBr \cdot CH_2 \cdot CO \cdot O' = {}'O \cdot CO \cdot \underset{\underset{O---CO}{|}}{CH} \cdot CH_2 + Br',$$
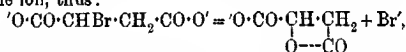
and the lactone ion then reacts with the hydroxyl ion, giving the ion of malic acid, thus:

$$'O \cdot CO \cdot \underset{\underset{O---CO}{|}}{CH} \cdot CH_2 + OH' = {}'O \cdot CO \cdot CH(OH) \cdot CH_2 \cdot CO \cdot O'.$$
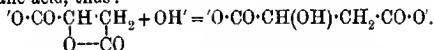
The reaction constants of both reactions are determined, the former being determined in neutral solution, using the sodium, potassium, barium, and strontium salts of the acid. The reaction constant is found to be $k = 0 \cdot 002403$, and is independent of the nature of the metal ion.

The addition of neutral salts causes the constant to increase slightly, but this is held to be due to the superimposing effect of the second reaction. The second reaction constant was determined in alkaline solution using the hydroxides of sodium, potassium, barium, strontium, both with and without the addition of the nitrate corresponding with the hydroxide. This reaction is shown to depend on the nature and concentration of the cation, and follows the empirical rule of Holmberg (*loc. cit.*): $C_M = C[M']a$. It is found that $d = \frac{1}{3}C_{Na} = 0 \cdot 095$ $C_K = 0 \cdot 093$; $C_{ba} = 0 \cdot 197$, and $C_{sr} = 0 \cdot 196$.   J. F. S.

Theory of Efflorescence. Influence of the Size of the Crystal. CH. BOULANGER and GEORGES URBAIN (*Compt. rend.*, 1912, 155, 1612—1614. Compare this vol., ii, 34).—Starting from their law $\log(m_t - m_t) = \log a + A \log(\theta - t)$, the authors deduce the equation $\log a' = \log a + (1 - A/3) \log p'/p$ for the relationship between the efflorescence of two crystals of weights p' and p respectively.

They have applied this to two crystals of sodium sulphate, and consider that the values found and calculated are in agreement within the limits of experimental error.   W. G.

Kinetics of Chemical Reactions of Combination, Deoxidation, and Oxidation. II. E. I. ORLOV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1576—1597).—Examination of Spitalsky's results dealing with the catalytic decomposition of hydrogen peroxide (A., 1911, ii, 36) in the light of the considerations previously advanced by the author (A., 1912, ii, 243) leads to the following conclusions.

The catalytic decomposition of hydrogen peroxide by chromic acid furnishes an example of the transformation of a unimolecular reaction of the first order into a unimolecular one of the second order. This transformation is conditioned by the action of an intermediate form of the oxide formed during the reaction and entering the sphere of the catalysis only after the peroxide is decomposed to a certain extent.

The influence of this intermediate form is complicated by the fact that one form of catalysis is converted into the other, not suddenly, but gradually; when the intermediate form comes into action, the coefficient f appears in the differential equation :

$$dx/dt = k(A - fx)(B + fx).$$

This appearance of f is dependent on the consumption of a certain proportion (one-fifth to one-eighth part of the original amount remains) of the hydrogen peroxide, and the consequent difficulty of oxidation of Cr^{III} to Cr^{VI}; a more rapid process of oxidising $Cr_2O_2(O_3H_4)_4$ to $Cr_2O_7H_2$ is then initiated, $Cr(OH)_7$ being formed as an intermediate product in the change. It is hence necessary to assume, in the kinetics of chemical processes, the principle of least loss of time; chemical processes strive to take place in such a way that there occurs the least waste of time.

The reducing properties of hydrogen peroxide are explained as due to the quadrivalency of oxygen in the molecules of the peroxide and of water. The oxidation of the hydrogen ions is regarded as a combination with the molecule $H \cdot O \vdots O \cdot H$, thus : $H \cdot O \vdots O \cdot H + 2H^{\cdot} = H_2 \vdots O \vdots O \vdots H_2 = 2 {}^{H}_{H} > O <$. The first stage of this reaction requires time, but the second proceeds instantaneously.

This hypothesis of the quadrivalency of oxygen necessitates the assumptions that aqueous solutions contain the complex, $H_2 \vdots O <^{O \vdots H_2}_{O \vdots H_2}$, possessing reducing properties, and that the ions Cr_2O_7'' and the molecules H_2O_2 give an intermediate oxide of the type

$$Cr_2O_3 \begin{bmatrix} -HO \\ -HO \end{bmatrix} > OH_2 \Big]_4 \quad \text{or} \quad Cr(OH)_7.$$
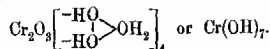
This oxide is the oxygen-carrier, and takes part in the conversion of Cr^{VI} into Cr^{III} and of the latter into Cr^{VI} again. After combination of the hydrogen ions with hydrogen peroxide, the remaining groups, $(Cr_2O_7) \cdots$, with free affinities, also combine with $H \cdot O \vdots O \cdot H$,

giving $H \cdot O \!\!=\!\! O \cdot H$, which is highly nnstable nnder tbe conditions of
$\underset{Cr_2O_7}{\diagdown \diagup}$

Spitalski's experiments (*loc. cit.*) and ⸢decomposes into Cr_2O_7'', $2H'$, and O_2, but is comparatively stable nnder the ordinary conditions of room-temperature and absence of vigorous shaking.

If the catalytic decomposition of hydrogen peroxide by means of potassium dichromate proceeds under ordinary conditions, the stable compounds $\underset{Cr_2O_7}{\overset{H \cdot O \!\!=\!\! O \cdot H}{\diagdown \diagup}}$ and $\underset{HCrO_4 \quad HCrO_4}{\overset{H \cdot O \text{———} O \cdot H}{| \qquad |}}$, are obtained, and the decomposition follows the differential equation: $dx/dt = k(A-x)(B+x)$. Tbis equation is applicable to reactions of combination. The form $dx/dt = k(A-x)$ represents a particular case.   T. H. P.

Kinetics of Chemical Reactions of Combination, Deoxida-tion, and Oxidation. III and IV. E. I. ORLOV (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1598—1623, 1623—1658).—The considerations advanced in previous papers (see preceding abstract) are applied to other reactions.

The decomposition of hydrogen peroxide by an iodide in aqueous solution is shown to be a unimolecular reaction of the second order, decomposition by means of potassium dichromate or molecular platinum proceeding similarly. The mechanism of these cbanges is discussed.
T. H. P.

Univereal Significance of the Elementary Quantum. OTTO SACKUR (*Ann. Physik*, 1913, [iv], 40, 67—86. Compare A., 1912, ii, 145, 1151).—By a process of reasoning similar to that adopted in the previous papers, equations have been deduced for the energy and entropy of ideal monatomic solid substances and of monatomic gases. The reasoning is based on a more precise definition of the (physical) conception of probability, and not on the usual assumption of elemen-tary energy quanta. The only quantities occurring in the equations are certain general constants, and also tbe atomic vibration frequency in the case of the solids and the molecular weight in the case of the gases.

The values of the "chemical constants," which determine the chemical behaviour of the gases and the vapour pressures of their condensation products, are calculated for helium, neon, argon, krypton, xenon, and mercury, In atmospheres, this constant C is given by the equation $C = -2 \cdot 055 + 1 \cdot 5 \log M$, where M is the molecular weight of the gas. It is shown that the calculated vapour pressures of mercury between $0°$ and $360°$ are in fairly good agreement with the observed values when the "constant" for mercury given by this equation is applied in the calculation of the vapour pressure curve. The calculated and observed vapour pressures of argon at $84°$ abs. are also concordant.   H. M. D.

The "Chemical Constants" of Di- and Tri-atomic Gases. OTTO SACKUR (*Ann. Physik*, 1913, [iv], 40, 87—106. Compare preceding abstract).—On the assumption that the di- and tri-atomic gases have

the structure assigned to them by Boltzmann, formulæ are deduced from which the entropy and the "chemical constants" of these gases may be calculated. The values obtained for hydrogen, oxygen, nitrogen, the halogen and halogen acids, carbon monoxide, nitric oxide, water, hydrogen sulphide, carbon dioxide and sulphur dioxide are recorded. The "chemical constants" are applied in the calculation of the vapour-pressure curves of iodine and ice, and of the dissociation constants corresponding with the equilibria: $2HCl \rightleftharpoons H_2 + Cl_2$, $2HBr \rightleftharpoons H_2 + Br_2$, $2HI \rightleftharpoons H_2 + I_2$, $2H_2O \rightleftharpoons 2H_2 + O_2$, $2CO_2 = 2CO + O_2$, and $2NO \rightleftharpoons N_2 + O_2$. From a comparison of the calculated vapour pressures and dissociation constants with experimental data, it is found that the values obtained for the "chemical constants" may be regarded in most cases as approximately correct. The existence of considerable discrepancies between theory and experiment which is found in certain cases, for example, the dissociation of carbon dioxide and nitric oxide, indicates, however, that the values of the "constants" cannot be regarded as final, and that it will probably be necessary to modify the theory of polyatomic molecules before the true values can be derived.

H. M. D.

Volume and Valency. M. SEBALDT (*Zeitsch. physikal. Chem.*, 1913, 81, 749—753).—A theoretical paper in which the relationship between valency and atomic volume and also other properties of the elements is shown to be periodic. In one diagram the logarithms of the atomic volumes are plotted as ordinates, the elements being placed on lines parallel to the ordinate axis which represent the eight groups of the periodic system. This arrangement shows clearly the relationship between the electroaffinity and the volume; atomic magnetism and compressibility are also shown to be functions of the atomic volume. In another arrangement the elements are placed round a polar co-ordinate ring in order of atomic weight, those of even valency to the left of the ordinate axis and those of odd valency to the right; the logarithm of the atomic volume is plotted on the ordinate. This arrangement brings out most of the relationships between the elements very clearly.

J. F. S.

The Nature of Auxiliary Valencies. II. Metal Ammonias. FRITZ EPHRAIM (*Zeitsch. physikal. Chem.*, 1913, 19, 513—538. Compare A., 1912, ii, 546).—The present paper contains further details on ammonia derivatives of the metal salts. It is shown that errors are likely to come into the pressure measurements of ammine derivatives, owing to incomplete drying and absorption of air by the finely divided compounds. Precautions for avoiding these errors are indicated. The gaseous pressure at a series of temperatures is determined for the hexammine derivatives of the halogen salts of cadmium, zinc, manganese, nickel, cobalt, iron, copper, calcium, and magnesium. It is found that the ratio T_{ci}/T_r is a constant for a given pair of salts at all pressures, where T is the temperature at which the two compounds have the same gaseous pressure. Compounds of this type, therefore, obey the Ramsay-Young rule. The value of the factor varies from 0.988 for $ZnI_2/ZnBr_2$ to 1.232 for $MnI_2/MnCl_2$. The temperature at

which the dissociation pressure of the various salts is 500 mm. is given, and it is seen that the pressure generally decreases as the atomic volume of the central atom increases.   The hexammines of zinc iodide, cupric bromide, and those of the chloride, bromide and iodide of cadmium being exceptional.   The value $\sqrt[3]{Tv}$ is shown to be constant for all the hexammines except those mentioned above, and in this connexion it is shown that taking the mean value of $\sqrt[3]{Tv} = 14\cdot0$, it is possible to calculate the atomic volume of the central atom with fair approximation when T is the absolute temperature at which the dissociation pressure is 500 mm.   It is found that when the absolute temperatures for pressures of 700 mm. and 200 mm. are taken the ratio is approximately constant ($1\cdot085 - 1\cdot073$).   Moduli are calculated for the pressure-temperature relationship of $I : Cl$, $I : Br$, $Br : Cl$, and from these it is seen that generally at a given temperature the tension is greatest for the chlorides and least for the iodides.   From calculations from the Nernst equation, $\log p = - Q/(4\cdot5717T) + 1\cdot75 \log T + 3\cdot3$, it is shown that the dissociation of the hexammines of the bivalent metals occurs by first splitting off one molecule of ammonia :

$$R''(X)_2 6NH_3 \rightleftharpoons R''(X)_2 5NH_3 + NH_3.$$
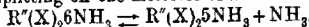
The heats of formation of the various ammines are calculated both from the Nernst formula and the van't Hoff formula. A series of notes on the preparation of the ammines used in the investigation is given.
J. F. S.

The Nature of Auxiliary Valencies. III.   The Region of the Existence of Auxiliary Valency Compounds. FRITZ EPHRAIM (*Zeitsch. physikal. Chem.*, 1913, **81**, 539—542. Compare preceding abstract).—The dissociation of the hydrates and ammines is theoretically considered.   It is shown that whilst the ammines dissociate by successively splitting off one molecule of ammonia this is not analogous to the hydrates. The reason is the formation of solutions in the case of the hydrates.   It is concluded that all the possible hydrates exist if only in a labile condition and in solution. It is also shown why the dissociation curves of the ammines show no transition points, whilst those of the hydrate do.   J. F. S.

What are Bases and Acids? DANIEL VORLÄNDER (*J. pr. Chem.*, 1913, [ii], **87**, 84—91).—Theoretical.   F. B.

New Shaking Apparatus. WILHELM STEINKOPF and HANS WINTERNITZ (*Chem. Zeit.*, 1913, **37**, 40).—The apparatus resembles a retort stand where the upright is fitted, by means of hall-bearings, into a heavy cast-iron base. A short horizontal arm is attached to the upright and connected with the eccentric of a small motor. The usual retort stand clamps may be used for holding water- and hot-air baths, and flasks for the distillation of viscous liquids which otherwise have a tendency to bump. The apparatus may also be used for holding burettes for the titration of boiling liquids.
On account of the gentle rotating movement imparted to the contents of the vessels, it is not necessary to use stoppers, and hence any risk of introducing impurities is avoided.   H. B. H.

Shaking Apparatus, which can be Exhausted, Fitted with an Inner Temperature Regulator. RICHARD KEMPF (*Chem. Zeit.*, 1913, **37**, 58—59).—A modification of the apparatus previously described (A., 1906, ii, 433), the principle remaining the same. The method by which the apparatus may be used in investigating catalytic reductions with colloidal or finely divided platinum is described.

T. S. P.

A Simple Experiment Illustrating the Luminosity of Phosphorus. DOUGLAS F. TWISS (*Chem. News*, 1913, 107, 16).—A vertical glass tube, 2—2½ cm. internal diameter and about 120 cm. long, is fitted at the lower end with an indiarubber bung carrying a glass tube, which is bent upwards so as to be parallel to, and of approximately the same height as, the wider tube. A solution of phosphorus in olive oil is introduced into the wider tube so as to reach about 6 inches from the top, and steady suction is applied at the mouth of this tube by means of a water pump. Air enters through the narrow tube, and a beautiful series of bell-shaped phosphorescent air bubbles rises through the column of oil.   T. S. P.


Inorganic Chemistry.

Early Work on Hydrofluoric Acid and the Isolation of Fluorine. FREDERICK D. CHATTAWAY (*Chem. News*, 1913, 107, 25—26).—Historical.

Reactions of Ozone with Certain Inorganic Salts. YOSHITO-YAMAUCHI (*Amer. Chem. J.*, 1913, 49, 55—68).—A study has been made of the action of ozone on certain inorganic salts with the object of ascertaining whether the oxidation is effected by only one oxygen atom of the ozone molecule or whether all three atoms take part in the process. A method has been devised by which each sample of ozonised oxygen can be divided into two parts, one for carrying out the experiment, and the other for analysis.

The salts employed included potassium arsenite, stannous chloride, sodium thiosulphate, thallous nitrate, mercurous nitrate, and ferrous ammonium sulphate. In the case of stannous chloride, the oxidation takes place according to the equation

$$3SnCl_2 + 6HCl + O_3 = 3SnCl_4 + 3H_2O,$$
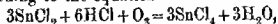
but in all the other cases only one oxygen atom of the ozone molecule reacts with the salt, the ozone decomposing, thus : $O_3 = O_2 + O$. When sodium thiosulphate is treated with ozone, two reactions occur, one involving the catalytic decomposition of the salt,

$$3Na_2S_2O_3 = 3Na_2SO_3 + 3S,$$
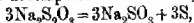
and the other effecting a partial oxidation of the sulphite formed, $2Na_2SO_3 + 2O_3 = 2Na_2SO_4 + 2O_2$. Thallous salts are rapidly and completely oxidised by ozone, and the thallic oxide produced can be readily

collected and weighed; the reaction is therefore applicable to the
estimation of ozone.
<div align="right">E. G.</div>

The Dynamic Allotropy of Sulphur. IV. Hugo R. KRUYT
(*Zeitsch. physikal. Chem.*, 1913, **81**, 726—748. Compare A., 1908,
ii, 1028; 1909, ii, 228, 802).—The paper is chiefly polemical. It is
shown that mixed crystals are formed by $S\mu$, and $S\lambda$, and that the
transition $S_{rh.} \dashrightarrow S_{mon.}$ takes place at a higher temperature in the
presence of $S\mu$. The transition point of pure $S_{rh.}$ is 95·3°, whereas the
generally observed transition point is 95·5°, and the triple point $S_{rh.}$
$S_{mon.}$ and $S_{liq.}$ lies at 95·9° ± 0·1°. Attempts are made to calculate the
transition point of rhombic sulphur on the basis of Nernst's theorem,
but this led to results which are in no way like the experimentally
determined values. An answer is given to the papers of Wigand
(A., 1910, ii, 602, 1055), Smits and Leeuw (A., 1912, ii, 40), Leeuw
(this vol., ii, 40), Preuner and Schupp (A., 1909, ii, 997), and to
Wo. Ostwald (*Grundriss der Kolloidchemie*, p. 132). The following
thermal constants of sulphur are collected in the paper; these are
held to be trustworthy.

M. p. monoclinic sulphur (free from $S\mu$), 119·25°.

M. p. monoclinic sulphur, as usually prepared, 114·5°.

M. p. rhombic sulphur (free from $S\mu$), 112·8°.

M. p. rhombic sulphur, as usually obtained, 110·2°.

M. p. of nacreous variety of sulphur (free from $S\mu$), 106·8°.

M. p. of nacreous variety of sulphur, as generally obtained, 103·4°.

Transition point $S_{rh.} \dashrightarrow S_{mon.}$ (free from $S\mu$), 95·3°.

Transition point usually obtained, 95·5° (3·1% $S\mu$ present).
<div align="right">J. F. S.</div>

**The Chemistry of the Formation of Nitric Oxide in the High
Tension Arc.** Franz Fischer and Emil Hene (*Ber.*, 1912, **45**,
3652—3658).—The purely thermal formation of nitric oxide from
nitrogen and oxygen has been questioned by various investigators (compare Haber and Koenig, A., 1908, ii, 34, 940 ; Grau and Russ, A., 1907,
ii, 753). Escales, in a discussion before the German Bunsen Society
(*Zeitsch. Elektrochem.*, 1906, **12**, 539), raised the question whether the
formation of nitric oxide might not be preceded by the activation of
the nitrogen, but Strutt has since shown (A., 1912, ii, 153) that active
nitrogen does not react with oxygen. The authors now show that the
energy of the discharge is probably used up in dissociating the oxygen
molecules, this being an endothermic process. Outside the arc the
following processes, which are exothermic, then take place: (1)
re-formation of molecular oxygen, (2) oxidation of molecular oxygen
to ozone, (3) formation of nitric oxide. The latter may be a direct
reaction between the active oxygen atoms and the nitrogen, or may be
due to a reaction between the ozone and the nitrogen, which reaction
would be exothermic.

The above conclusions are based on the following experiments.
When pure oxygen is sparked as it passes out of a quartz capillary and
mixes with pure nitrogen in a closed apparatus, six and a-half times more
nitric oxide is produced than when the nitrogen is sparked and mixes with

oxygen. Similarly, when air is sparked and blown into oxygen, four times as much, when blown into nitrogen, twice as much, nitric oxide is produced as when pure nitrogen is sparked and blown into pure unsparked oxygen.

A high-tension arc was produced in a quartz apparatus cooled with water. When air was sent through the arc and then mixed immediately with oxygen, air, and nitrogen respectively, the volume percentages of nitric oxide produced were respectively 7·8, 7·4, and 5·9.

When air is submitted to the silent discharge in a quartz Siemens ozone tube heated at varying temperatures (20—700°), the percentage of nitric oxide produced increases with rise in temperature, owing to the increased velocity of reaction between any ozone produced and the nitrogen, reaction taking place before the ozone is destroyed by the high temperature.

The above results indicate that better results would be obtained on a manufacturing scale if oxygen were passed through the arc flame instead of air, using magnotite electrodes, and then rapidly mixed with nitrogen and cooled.   T. S. P.

The Inner Cone of Hydrocarbon Flames.   FRITZ HILLER (*Zeitsch. physikal. Chem.*, 1913, 81, 591—625. Compare A., 1910, ii, 122).—A further investigation of the inner cone of certain flames. The ether and coal-gas flames are chiefly investigated, and the analyses of the products of combustion at the point of the cone, the side of the cone, and at different positions above the cone in the space between the inner and outer cone are made. Temperature determinations were made by means of an iridium, iridium-rhodium couple, and these values were compared with the temperatures calculated from the composition of the gas in the space between the two cones and the known specific heats and heats of combustion on the one hand, and with those obtained from the equilibrium constant and its relation to temperature on the other.

Considerable difficulty was experienced in the calculations owing to the uncertainty of the thermal data required for obtaining the temperature. The constant $K = (H_2O/CO_2) \cdot (CO/H_2)$ is given for all experiments, the various values being obtained by gas analytical processes. The equilibrium constant is found to be about 3·4 when the gases coming from the inner cone are cooled to a temperature which allows of no further change, but when the coal gas has been previously mixed with carbon dioxide, the equilibrium constant is considerably lower than 3·4. In the case of the ether flame, this constant is often found to be as low as 2·8, the higher value only being obtainable when a very small flame is employed.   J. F. S.

The Various Forms of Silica and their Mutual Relations. CLARENCE N. FENNER (*J. Washington Acad. Sci.*, 1912, 2, 471—480).— The velocity of transformation of one form of silica into another is extremely slow, and the different forms may exist together over considerable ranges of temperature. The inversions may be hastened

by employing a catalytic agent (sodium tungstate). The following inversion points were determined from the heating curves :

a-Quartz (tetartobedral hexagonal) $\rightleftarrows$ β-quartz (hemibedral hexagonal), 575°.

β Quartz $\rightleftarrows$ β-tridymite (holohedral hexagonal), 870° ± 10°.

β-Tridymite $\rightleftarrows$ β-cristobalite (cubic), 1470° ± 10°.

On cooling, β-tridymite and β-cristobalite promptly pass at the following temperatures into metastable forms possessing lower optical symmetry :

β-Tridymite $\rightleftarrows$ a-tridymite (biaxial, perhaps orthorhombic), 115—120°.

β-Cristobalite $\rightleftarrows$ a-cristobalite (biaxial), 180—270°.

Chalcedony possibly represents a seventh form of silica.   L. J. S.

The Transformations of Silica at High Temperatures. KURD ENDELL and REINHOLD RIEKE (*Zeitsch. anorg. Chem.*, 1912, 79, 239—259).—The present investigation deals with pure temperature changes in the absence of mineralisers. The specimens of native silica, in fragments of 1—3 c.c. and also in powder, are heated in an electric furnace, and the direction of the transformation determined by measurements of the density, using the data D (quartz) 2·65, (cristobalite) 2·33, (silica glass) 2·21.

Quartz and chalcedony which have been heated at 1450° have often been described as optically isotropic, owing to the microscopic cracks produced during the transformation, which also give rise to an error in the determinations of density. Cristobalite is best recognised by its change of volume at about 230°, measured in a mercury dilatometer. This is the only means of distinguishing it from tridymite.

Quartz and amorphous silica are converted into cristobalite by heating above 800°, but an exact temperature of transformation has not been found. The velocity of conversion increases with the temperature. Between 1200° and 1600° the transformation of silica glass is proportional to the time. Twinned quartz is converted more rapidly than simple crystals, and chalcedony still more rapidly. Using an iridium furnace, β-cristobalite is found to have m. p. 1685° ± 10°.

The factor determining the rate of transformation is the extent of surface, a twinned crystal having a greater effective surface than a simple one, and fibrous varieties, such as chalcedony, a still greater surface. The quartz of pegmatite and graphic granite is often repeatedly twinned. Chalcedony may be regarded as an unstable transitional form of quartz. Massive rock crystal may probably be melted by rapid heating, without previous conversion into cristobalite. The present data do not allow of the construction of an equilibrium diagram for silica, but an attempt is made to classify the various modifications in accordance with Tammann's hypothesis (A., 1912, ii, 149).   C. H. D.

Capacity of Potassium Haloids for Forming Solid Solutions at High Temperatures. MARIO AMADORI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 606—610. Compare A., 1912, ii, 758).—The author has repeated some of his former experiments with results which con-

firm those obtained by him and Pampanini (A., 1912, ii, 48), and do not agree with those of Vrshesnevsky (A., 1912, ii, 137). The author's conclusions are further supported by recent work of Nacken and Schobert (*Diss.*, Leipzig, 1912) and Nacken and Flack (unpublished).

R. V. S.

Some Properties of Alkali Nitrites. MARCEL OSWALD (*Compt. rend.*, 1912, **155**, 1504—1506).—The author has prepared sodium and potassium nitrites in a high state of purity and examined their properties. Sodium nitrite, when heated in a vacuum, melts at 217° (compare Divers, T., 1899, **75**, 86) and decomposes at 320°; potassium nitrite melts at 297·5° and decomposes at 350°. After fusion and resolidification they have respectively D_4^0 2·168 and 1·912. The densities of their solutions at various concentrations are given.

W. G.

The Silver–Zinc Equilibrium. HENRY C. H. CARPENTER and W. WHITELEY (*Internat. Zeitsch. Metallographie*, 1912, **3**, 145—169). —The equilibrium diagram given by Petrenko (A., 1906, ii, 284) is incompatible with the phase rule. It is shown that the errors in the diagram are due to the use of insufficient quantities of material, to want of uniformity, and to the absence of proper annealing. The system has now been reinvestigated, using larger quantities and employing greater precautions. The actual diagram is of a much simpler character. The liquidus has been determined accurately by Heycock and Neville (T., 1897, **71**, 407). The limits of the α-solid solution at 220° (determined on samples annealed for six weeks) are 100 and 62·7 atomic % of silver. The β-constituent is unstable below 264°, at which temperature there is a eutectoid point, $\beta \longrightarrow \alpha + \gamma$. The γ-constituent is the compound Ag_2Zn_3; it is highly brittle and develops conspicuous cleavage cracks. At 220° the γ-range is from 40 to 37·3 atomic % Ag. The δ-constituent (probably Ag_2Zn_5), which is also brittle, has a range 29 to 14·3 atomic % Ag, whilst the η-constituent is confined to the immediate neighbourhood of the zinc end of the series. The ε-constituent does not exist below 310°. There is thus a very close resemblance, throughout the whole system, between the copper–zinc and silver–zinc series.

C. H. D.

The Copper–Zinc, Silver–Zinc, and Silver–Cadmium Equilibria HENRY C. H. CARPENTER (*Internat. Zeitsch. Metallographie*, 1912, **3**, 170—175).—A remarkable similarity is observed between the equilibria in the systems copper–zinc (A., 1912, ii, 764), silver–zinc (preceding abstract), and silver–cadmium (Petrenko and Fedorov, A., 1911, ii, 281, 800).

In each case a compound of similar composition,

$$Cu_2Zn_3, \ Ag_2Zn_3, \ Ag_2Cd_3,$$
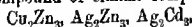
determines the form of the diagram. The α-solid solutions have a similar range of stability, and near to the compositions CuZn, AgZn, and AgCd, β-constituents occur, having a comparatively wide range of composition at a high temperature, narrowing with falling temperature until a eutectoid point is reached at or about 50 atomic %. The γ-constituent is in each case the pure compound. It is remarkable

that the systems copper–tin and copper–aluminium also include a
β-constituent stable only above a certain temperature, and then
undergoing a eutectoid inversion.

The copper–cadmium diagram does not show any close analogy
with the above.   C. H. D.

The Preparation and Investigation of Silver Oxide. E. Hösr
MADSEN (*Zeitsch. anorg. Chem.*, 1912, 79, 195—201).—Silver oxide has
not hitherto been obtained in a pure condition. A concentrated
solution of silver nitrate is precipitated with a dilute solution of
sodium hydroxide, and the precipitate is washed with water, previously
freed from carbon dioxide. It is then dried at 85—88° in a stream
of air free from carbon dioxide. The product contains 1·75% of
silver hydroxide (0·125% of water), and about 0·5% of silver carbonate.
Some reduction takes place, as, whilst the moist precipitate yields a
white chloride with hydrochloric acid, even after exposure to light, the
dry solid always yields a red chloride, the colour of which is deeper
the higher the temperature of drying.

The oxide dried at 85° is dark brown with a violet shade. At 280°
the water is almost completely expelled, but it is not possible to obtain
a product of constant weight, as appreciable dissociation of the oxide
takes place.   C. H. D.

Cement Limeetones of Santa Marinella. NICOLA PARRAVANO
(*Gazzetta*, 1912, 42, ii, 610—617).—The paper records analyses of a
number of specimens from this district (which lies south of Civita-
vecchia) carried out to determine the suitability of the stones for the
manufacture of Portland cement, and gives the results of tests applied
to the cements made from them.   R. V. S.

Gelatinous Calcium Sulphate and the Setting of Plaster.
CAVAZZI (*Gazzetta*, 1912, 42, ii, 626—632).—When calcined calcium
sulphate is treated with water, a gelatinous calcium sulphate is first
formed, which in a few minutes at low temperatures, and more rapidly
at higher temperatures, turns into crystals of $CaSO_4,2H_2O$. The
gelatinous salt can be observed to crystallise under the microscope,
and it is identical with that produced by the addition of alcohol to a
supersaturated solution of calcium sulphate. That the setting of
plaster is not due to the crystallisation of $CaSO_4,2H_2O$ from a super-
saturated solution is shown by the fact that the increase of volume on
setting is very much less than that which is found to occur when the
salt is allowed to crystallise from a supersaturated solution.

R. V. S.

**The Rôle of Calcium Sulphate and Barium Sulphate in the
Reduction of Zinc Minerals.** EUGÈNE PROST and MAURICE URAGH
(*Bull. Soc. chim. Belg.*, 1912, 26, 532—541. Compare A., 1911, ii,
283).—In the presence of silica the sulphates of calcium and barium
have a marked influence on the reduction of zinc minerals. They
consume a large amount of heat for their decomposition or reduction
and, in the presence of silica, react with it generating sulphurous

vapours, which in contact with the zinc vapour cause the formation of zinc sulphide, which remains in the distillation residue, thus increasing the loss of zinc, the sulphide only being reduced at a much higher temperature. The presence of silica is necessary for the formation of zinc sulphide, as, in its absence, the calcium and barium sulphides formed by the reduction of the corresponding sulphates do not yield their sulphur to the zinc oxide of the roasted blende at the experimental temperature of 1200° (compare *Metallurgie*, 1911, 8, 763).

W. G.
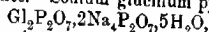
Glucinum Phosphates, and Glucinum Phosphite and Hypophosphite. BENNO BLEYER and BR. MÜLLER (*Zeitsch. anorg. Chem.*, 1912, 79, 263—276. Compare A., 1912, ii, 644).—*Mono-glucinum orthophosphate*, $GlH_4(PO_4)_2$, prepared from the hydroxide and orthophosphoric acid, forms colourless, hygroscopic leaflets. Diglucinum orthophosphate, $GlHPO_4,3H_2O$, has not been obtained free from adhering phosphoric acid. *Triglucinum orthophosphate*, $Gl_3P_2O_8,6H_2O$, obtained from disodium phosphate, acetic acid, and glucinum sulphate, forms a loose precipitate. A basic *salt*,

$$2Gl_3P_2O_8,GlO,13H_2O,$$
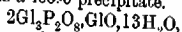
is obtained when trisodium phosphate is used for precipitation.

Potassium glucinum orthophosphate, and also the corresponding sodium and ammonium salts, have only been obtained as precipitates of variable composition. The glucinum phosphates previously described in the literature are mixtures.

Glucinum pyrophosphate, $Gl_2P_2O_7,9H_2O$, is precipitated by means of sodium pyrophosphate. Sodium glucinum pyrophosphate,

$$Gl_2P_2O_7,2Na_4P_2O_7,5H_2O,$$

is a soluble, hygroscopic salt. *Glucinum metaphosphate*, $Gl(PO_4)_2$, forms colourless crystals, and must be prepared in absence of water, otherwise a basic salt is obtained. Glucinum phosphite,

$$4GlHPO_3,GlO,7H_2O,$$
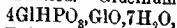
and hypophosphite, $GlH_4P_2O_4$, have also been prepared.   C. H. D.

Magnesium Ions as Oxygen Carriers. OTTO HAUSER (*Chem. Zeit.*, 1913, 37, 58).—The rusting of iron is accelerated by the presence of magnesium ions. In general, reactions which take place with absorption or evolution of oxygen are similarly accelerated. The effect of magnesium ions is best shown in the oxidation of hydrochloric acid or chlorides by permanganate.   T. S. P.

Thermal Analysis of Binary Mixtures of Chlorides of Bivalent Elements. IV. CARLO SANDONNINI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 634—640. Compare A., 1912, ii, 1172).—The present paper deals with the thermal analysis of the systems $MgCl_2$–$SrCl_2$, $MgCl_2$–$BaCl_2$, and $MgCl_2$–$MnCl_2$. The magnesium chloride used contained 1·11% of oxide, which was allowed for in calculating the compositions of the mixtures dealt with.

Magnesium chloride and strontium chloride do not seem to form solid solutions; there is an eutectic corresponding with 535° and 0 mols. % of strontium chloride.

The system $MgCl_2$–$BaCl_2$ is analogous to the system $MnCl_2$–$BaCl_2$ already studied. There is an eutectic corresponding with 36 mols. % of barium chloride and about 556°. Mixtures containing more barium chloride show a pause at 590°, as well as that of the eutectic; if the amount of barium chloride is increased, only this upper pause is observed, but if the amount is still further raised the pause falls again until it coincides with the eutectic. These indications point to the production of a compound decomposing on fusion.

Magnesium chloride and manganese chloride are completely soluble both in the solid and in the liquid state, and mixtures of them melt at temperatures intermediate between those of the constituents.

The author discusses the regularities which may be perceived in the thermal behaviour of the binary mixtures of chlorides of bivalent elements investigated by himself and others.   R. V. S.

[Metastable Metals.] E. B. WOLFF (*Zeitsch. Elektrochem.*, 1913, 19, 19—23. Compare Cohen, A., 1909, ii, 1008).—Polemical. The author shows that an etching solution does not convert a metal, which has been rendered metastable by deformation, into the stable condition. The action is shown to be the removal of the deformed and metastable surface layer with the exposure of the stable underneath layer.

It is also stated in opposition to Cohen (*loc. cit.*) that a metal which has been rendered stable by etching is unable to innoculate other metal which has been subjected to deformation.   J. F. S.

[Metastable Metals.] ERNST COHEN (*Zeitsch. Elektrochem.*, 1913, 19, 23).—Polemical. An answer to Wolff (preceding abstract).
        J. F. S.

Physico-chemical Studies on Red Lead. JAROSLAV MILBAUER (*Chem. Zeit.*, 1912, 36, 1436—1437, 1484—1485).—By means of a specially designed apparatus the author has investigated the formation of red lead from lead oxide under oxygen pressures varying from 1 to 12 atmospheres, and at temperatures from 325° to 520°. The results show that the equilibrium is independent of the pressure, but is attained more rapidly with increasing pressure. One hundred % of red lead is formed at 470—480°, the percentages being less above and below this temperature, the time of experiment being in all cases three hours.   T. S. P.

The Structural Resolution of the Pure Copper-Zinc β-Constituent into α + γ. HENRY C. H. CARPENTER (*J. Inst. Metals*, 1912, 8, 51–58).—The β-constituent of alloys of copper and zinc, which undergoes transformation at 470° during cooling (A., 1912, ii, 764), does not segregate even after annealing for several months at 445°, although the presence of minute quantities of either the α- or γ-constituent brings about segregation much more rapidly. Repeated quenching in liquid air brings about the transitory development of a duplex structure, the nature of which is unknown. Resolution of the β-alloy at 445° is brought about by contact with an αγ-alloy of copper and zinc containing 0·95% of vanadium.   C. H. D.

The **Effect of Other Metals on the Structure of the** β-Constituent in Copper-Zinc Alloys. HENRY C. H. CARPENTER (*J. Inst. Metals*, 1912, 8, 59—85).—The resolution $\beta \longrightarrow a + \gamma$, which takes place in alloys of copper and zinc at 470° (A., 1912, ii, 764), is affected by the presence of other metals in the alloy. Metals which are insoluble in the solid alloy, such as lead and chromium, are without influence, but bismuth has been found in one case to accelerate the resolution Antimony, tin, aluminium, silicon, and vanadium, which enter into solid solution, displace the eutectoid composition to the γ side, and assist the resolution. Iron has much less effect. Nickel and manganese have little effect.　　　　　　　C. H. D.

Copper-Zinc-Nickel Alloys. LÉON GIULLET (*Compt. rend.*, 1912, 155, 1512—1514. Compare A., 1905, ii, 168).—A study of the influence of nickel when added to certain brasses. It is found that the addition of nickel considerably improves their mechanical properties and gives them a "fictitious" proportion of zinc considerably higher than their real proportion (compare A., 1906, ii, 357).
　　　　　　　W. G.

Constitution of Aluminates. EDWARD G. MAHIN, D. C. INGRAHAM, and O. J. STEWART (*J. Amer. Chem. Soc.*, 1913, 35, 30—39).—The solubility of aluminium hydroxide in alkali hydroxide solutions and the existence of minerals containing the oxides of aluminium and certain other metals in apparently constant proportions have led to the hypothesis that aluminium hydroxide is amphoteric. Most of the investigations on the aluminates have been directed to the determination of their formulæ, and have given varying results; they have also shown that the quantitative relations between the alkali metal and aluminium differ according to the method of preparing the solution. In view of these facts the present work was undertaken in order to ascertain whether the solubility of aluminium hydroxide in alkali hydroxides is not due rather to its colloidal properties than to its amphoteric character.

Measurements of the heat of solution of aluminium hydroxide in solution of sodium hydroxide, a quantitative study of the action of ammonium nitrate on a solution of sodium aluminate, and observations on the behaviour of sodium aluminate on electrolysis have been made. The results indicate that the solubility of aluminium hydroxide in alkali hydroxide solutions depends very largely on its colloidal properties, and that it is doubtful whether aluminates have any existence as definite salts.　　　　　　　E. G.

The Heusler Ferromagnetic Alloys of Manganese. FRIEDRICH HEUSLER (*Zeitsch. angew. Chem.*, 1912, 25, 2651—2653).—A claim for priority against Wedekind (this vol., ii, 55).　　　　　C. H. D.

The Formation of Nitrogen Oxides by Heating Manganese Dioxide in Air. PAUL ASKENASY and E. L. RÉNYI (*Zeitsch. Elektrochem.*, 1913, 19, 23—32).—The statement made by Odier (*J. phys. chim.*, 1798, 464) that oxides of nitrogen are produced when manganese

dioxide is heated in oxygen is investigated.   The authors heated natural and artificial manganese dioxide in a current of air at various temperatures.   It was found that very small quantities of oxides of nitrogen were evolved, which never amounted to more than 0.2 mg. nitric oxide from 10 grams of manganese oxide.   The oxides made their appearance at 280°, but on heating for several hours ceased to be formed.   On raising the temperature, a fresh quantity was produced. Above 700° no oxide could be obtained.   The authors draw the con- clusion that the oxides of nitrogen are not formed from atmospheric nitrogen, since the same results could be obtained by substituting a current of carbon dioxide for that of air.   They are of the opinion that the nitrogen is furnished by the manganese dioxide, which probably contains a nitrogen compound to the extent of 0.002%.

J. F. S.

The Passive State of Iron.   JAMES MacLEOD-BROWN (*Chem. News*, 1913, 107, 15).—It is frequently asserted that, if part of an iron nail or wire is rendered passive, the remainder of the nail or wire also assumes this state.   That this is not so may be shown as follows : An iron nail, three inches long, is immersed to a depth of one inch in con- centrated nitric acid.   The nail is allowed to drain, and the other end immersed to a depth of one inch in dilute nitric acid, when it will be found to be active ; the passive end remains passive.   If the nail is lowered into the dilute nitric acid, passive end first, the whole of it becomes passive after a short time.

Other experiments are described in which it is shown that when a passive iron nail is connected by means of a platinum or copper wire to a nail of ordinary iron, the two nails being immersed in dilute nitric acid, that part of the ordinary iron which dips into the nitric acid becomes passive after a short time, the passivity being produced by anodic polarisation.

The author considers that the passive state is conditioned by some definite arrangement of the particles at the surface of the iron.

T. S. P.

Equilibria in Quaternary Systems.   VI.   Quaternary Alloys of Iron, Nickel, Manganese, and Copper.   NICOLA PARRAVANO (*Gazzetta*, 1912, 42, ii, 589—609.   Compare A., 1912, ii, 1175 ; this vol., ii, 33, 55, 58).— In the present paper, which does not lend itself to abstraction, the author summarises the results which he has already obtained (*loc. cit.*) in the thermal study of the binary and ternary systems included in the above quaternary system, and referring to a former theoretical discussion of quaternary systems (this vol., ii, 33), he establishes theoretically the characteristics which should be displayed by this quaternary system.   The experimental part, which is accompanied by numerous tables, diagrams, and photomicrographs, gives the results of the experimental verification of these theoretical previsions.

R. V. S.

Determination of the Atomic Weight of Uranium.   WILLIAM ŒCHSNER DE CONINCK (*Compt. rend.*, 1912, 155, 1511—1512).—A

determination of the atomic weight of uranium by ignition of anhydrous uranyl oxalate, and weighing the residual uranium dioxide. The mean of seven determinations gives the value 238·4 for the atomic weight of uranium.   W. G.

The Oxides of Uranium. WILLIAM ŒCHSNER DE CONINCK and ALBERT RAYNAUD (*Bull. Soc. chim.*, 1912, [iv], 11, 1037—1038).— When uranium formate, covered with a layer of methyl alcohol, is exposed to the action of diffused daylight for three months, uranous oxide (UO_2) is deposited and formic acid formed.

When uranous oxide is heated in the air to a bright red heat, the oxide U_4O_{10} is produced.   T. S. P.

The Basicity of the Tungsto-acids. HIPPOLYTE COPAUX (*Compt. rend.*, 1913, 156, 71—75. Compare *Ann. Chim. Phys.*, 1912, [viii], 25, 22).—The author has determined the conductivity of acids of the type of phosphotungstic acid in very dilute solutions, and from his results deduced the basicity of the acids. Silicotungstic acid is tetrahasic, and even at high orders of dilution is practically unhydrolysed. Its isomeride, tungstosilicic acid, and its isomorph, silicomolybdic acid, are also tetrabasic and not hydrolysed on dilution. Borotungstic acid is pentabasic, this being in agreement with its known sodium, barium, and cadmium salts. Metatungstic acid is hexabasic, but is appreciably hydrolysed in very dilute solutions. Phosphotungstic acid is freely hydrolysed on dilution, and whilst the composition of its ordinary salts and its analogy to other acids point to its being tribasic, tho conductivity seems to reach a limit for a basicity of five. Phosphomolybdic acid is tribasic, but in moderately dilute solutions gives values for a tetrabasic acid, seemingly due to hydrolysis of the acid yielding two dibasic acids, which the author suggests is represented by the equation :

$$H_3[P(Mo_2O_7)_6H_4] + 2H_2O = H_2[P(Mo_2O_7)_5(OH)_2H_5] + H_2Mo_2O_7.$$
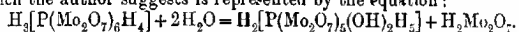
In general, the composition of the soluble salts of strong bases is a criterion of the basicity of tungsto- and molyhdo-acids, and the value so obtained is in accord with that obtained by conductivity methods. Disagreement is a sign of hydrolysis of the acid on dilution.
                                                        W. G.

The System Tin. ANDREAS SMITS and H. L. DE LEEUW (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 676—681).—The probable existence of a transition point for tin in the neighbourhood of 200° is indicated by a number of observations, and in particular by the experiments of Werigin, Lewkojev, and Tammann (*Ann. Physik*, 1903, [iv], 10, 147) on the rate of flow of tin under pressure.

The fact that Cohen and Goldschmidt (A., 1905, ii, 168) obtained no evidence of the existence of the transition point in dilatometric experiments is now shown to he due in all probability to the slowness with which the change in question takes place, and new observations with a dilatometer are recorded which indicate that the temperature of the reversible change tetragonal tin ⇌ rhombic tin is 202·8°. Small

quantities of mercury act as a catalyst, but at the same time the transition temperature is depressed

In the presence of 0·12 and 0·22% of mercury, 'the temperatures obtained by the dilatometric method were 173° and 151° respectively. The occurrence of this change at 202·8° accounts for the brittleness developed when tin is heated to about 200°

The transition temperature of 170° deduced by Cohen and Goldschmidt from the flow experiments referred to above, is based on an erroneous interpretation of the data in question, there being no evidence whatever for the occurrence of any change at this temperature.   H. M. D.

The System Tin–Iodine. H. S. VAN KLOOSTER (*Zeitsch. anorg. Chem.*, 1912, 79, 223–229. Compare Reinders and de Lange, this vol., ii, 60).—Stannous iodide, SnI_2, m. p. 321°, is practically immiscible with molten tin at 400°. Stannic iodide, SnI_4, m. p. 143°, mixes in all proportions with iodine, the eutectic point being at 12 atomic % of tin and 76°. Stannous iodide is only slowly formed from its components, even at 440° in a sealed tube.

Stannous iodide crystallises in ruby-red needles, D_{15}^{15} 5·21. Crystallographic measurements [by F. M. Jaeger] show that the crystals are monoclinic, $a : c = 1 : 0·5911$, $\beta = 82°55''$.   C. H. D.

Thorium Compounds. FRANZ HALLA (*Zeitsch. anorg. Chem.*, 1912, 79, 260—262).—A mixture of anhydrous thorium sulphate and magnesium carbonate with a little water yields a sandy precipitate of *basic thorium sulphate*, $ThOSO_4,5H_2O$. The same salt is obtained as a flocculent precipitate by the action of magnesium sulphate on a boiling solution of thorium sulphate or nitrate. The titration of thorium nitrate with potassium hydroxide and phenolphthalein is complete when 3·5 mols. KOH are present for 1 atom Th. With the basic sulphate the hydrolysis proceeds to the same stage:

$$ThOSO_4 : KOH = 1 : 1·75.$$

It is not possible to wash thorium hydroxide free from sulphate by means of dilute ammonia.

The addition of ammonium carbonate to a mixed solution of magnesium chloride and thorium nitrate yields a transparent emulsion, the globules of which change to a hard glass on drying. Magnesium hydroxide and thorium sulphate, or magnesium sulphate and thorium hydroxide, yield an opalescent jelly.   C. H. D.

The Preparation of Metallic Vanadium. III. WILHELM PRANDTL and HERMANN MANZ (*Zeitsch. anorg. Chem.*, 1912, 79, 209—222. Compare A., 1909, ii, 1022 ; 1910, ii, 1075).—The vanadium obtained by Ruff and Martin (A., 1912, ii, 166) by heating the trioxide with carbon in an electric vacuum furnace is only apparently purer than that obtained by the aluminothermic process, the slag which is always present having been deducted in the course of Ruff's analyses.

The addition of calcium fluoride in the aluminothermic process is not essential. Vanadium pentoxide gives better results than the

trioxide, the higher temperature obtained favouring the elimination of slag. The presence of alkali is harmful, as alkali vanadate passes into the slag, and 'an excess of aluminium remains. The attempt has been made to remove oxygen from the product by the addition of vanadium hydride, prepared by heating electrolytically disintegrated vanadium in hydrogen at 1000° (Muthmann, Weiss, and Riedelbauch, A., 1907, ii, 781), but a hydride has not been obtained, the increase in weight being due merely to combination with oxygen and nitrogen.

The reduction of vanadium trichloride with sodium in slight excess also yields a product containing about 96% of metal. Aluminothermic vanadium (95%) has D_{20} 5·987, and 96% metal from the chloride and sodium has D_{20} 5·819.　　　　　　　　　　　　　　　　　　　C. H. D.

The **Annealing of Coinage Alloys.** Thomas K. Rose (*J. Inst. Metals*, 1912, **8**, 86—125).—The softening of metals and alloys hardened by mechanical treatment takes place at any given temperature at first rapidly and then more slowly, but at temperatures approaching the melting point it is almost instantaneous. The change is accompanied by recrystallisation. The formation of new crystals, at 200° in the case of gold, is too rapid to be accounted for by diffusion. The softening is accompanied by expansion, which is greater in alloys than in pure metals.　　　　　　　　　　　　　　　　　C. H. D.

Condition of Gold in Gold Quartz. P. P. von Weimarn (*Zeitsch. Chem. Ind. Kolloide*, 1912, **11**. 287—290).—If 0·1 to 1% solutions of sodium auric chloride and sodium silicate are mixed, a clear solution is obtained, which gradually develops a reddish colour, and this changes slowly and finally becomes blue. Coagulation commences after several months, and the microscopic examination of the coagulum has shown a close similarity in structure with that presented by the gold in auriferous quartz.　　　　　　　　　　　　　　　　　H. M. D.

Some **Anomalies Observed in the Assay of Platinum Ores from Ural.** H. C. Holtz (*Ann. Chim. Phys.*, 1912, **27**, 559—566).—The process employed is briefly as follows : the mineral is treated with *aqua regia*, which leaves a residue composed of sand and a compound of osmium and iridium. The solution is evaporated to dryness, the residue treated with hydrochloric acid, and again evaporated and dried at 130° to reduce the iridium chloride to the ous-state. After dissolving in water, the platinum is precipitated quantitatively by addition of excess of ammonium chloride, and from the filtrate the other metals (iron excepted) are then precipitated by adding a little hydrochloric acid and a sufficiency of pure zinc.

After weighing, the deposit ("blacks") is treated with dilute nitric acid (1 : 1), which dissolves the palladium and copper. From this solution the palladium is precipitated by means of mercuric cyanide ; the excess of mercury is got rid of by ignition, preferably after evaporation with hydrochloric acid, and the copper precipitated finally as copper thiocyanate. Now, on applying the process to a mixture of the chlorides of platinum, iridium, palladium, rhodium, and copper, the

results were quite satisfactory, but when assaying the " Ural ore " the following anomalies were observed.

(1) The "blacks" are not totally dissolved by the nitric acid. (2) The copper oxide (after expelling the excess of mercury) is not completely soluble in hydrochloric acid. (3) The filtrate from the copper thio-cyanate is yellow, and gives a dark precipitate on addition of zinc. From further experiments it seems that : (a) The oxide of this mysterious substance is insoluble in hydrochloric, nitric, nitrohydrochloric, and sulphuric acid. (b) The oxide dissolves in aqueous sodium hydroxide with a yellow colour. This solution remains bright yellow on adding hydrochloric acid, and does not react with potassium iodide ; stannous chloride decolorises it. (c) When fused with oxidising mixture the oxide is not attacked and a colourless mass is obtained. (d) The dark product (3) is reduced to metal by ignition in a current of hydrogen, with slight loss in weight. (e) The metal is dissolved by melting with potassium hydrogen sulphate, yielding a brownish-red mass which does not give a white turbidity with water (absence of rhodium). (f) It is soluble in nitric acid, and its hydrochloric acid solution is not precipitated by ammonium chloride.

These properties taken in conjunction with similar experiences of other writers lead the author to believe that another unidentified element is present in the Ural ore.   L. DE K.

Mineralogical Chemistry.

The Native Elements of the Earth's Crust.   VLADIMIR I. VERNADSKI (Centr. Min., 1912, 758—765).—The author reproduces with some modifications and extensions a table from his recent Russian treatise on mineralogy (Opuit Opisatelnoï Mineralogii, part I. St. Petersburg, 1908). The main headings in this table are : (I) Solid crystalline chemical elements, A, metals, B, metalloids ; (II) solid colloidal elements ; (III) fluid elements ; (IV) gaseous elements. By including such modifications and combinations as α-, β-, and γ-ferrite, α- and β-ferroplatinum, bismuth-gold, etc., this list is extended to 106 minerals found in the state of native elements. The following forty-seven chemical elements as such occur native : Ag, Ar, As, Au, Bi, Br, C, Cd, Cl, Co, Cr, Cu, Fe, H, He, Hg, Ir, I, K ?, Kr, Mo, N, Na ?, Ne, Ni, O, Os, P ?, Pb, Pd, Pt, Ra ?, Ru, S, Sb, Se, Si ?, Sn, Ta, Te, Tl, Zn, Xe, thorium emanation and actinium emanation.
                L. J. S.

Optical Investigation of Ural Naphtha.   MICHAEL A. RAKUZIN (J. Russ. Phys. Chem. Soc., 1912, 44, 1737—1738).—A sample of naphtha from Dos-Sor, D^{15} 0·8754, showed distinct dichroism, had a carbonisation constant (K) in benzene (200 mm.) of 3·75—4%, and yielded distillates which were in all cases inactive. The naphtha is regarded as a perfect natural filter-distillate, and the lack of distillate below 150° indicates communication with the atmosphere.
                T. H. P.

White Sublimates of the Volcano Chinyero (Canaries). ANGEL DEL CAMPO (*Anal. Fis. Quim.*, 1912, 10, 431—449). —The sublimates arising from the eruption of November, 1909, are pale yellow, or pure white, crystalline masses interspersed with specks of lava, and consist of ammonium chloride (96·20%), ammonium fluoride (2·45%), ferrous chloride (0·25%), and chlorides of magnesium, aluminium, etc. (0·70%). Spectrographic examination revealed traces of tin, lead, silver, titanium, manganese, sodium, and, perhaps, tantalum.   G. D. L.

An Aluminium Arsenate from Utah. FRANK W. CLARKE (*J. Washington Acad. Sci.*, 1912, 2, 516—518).—A white, amorphous mineral found with orpiment in the Sunshine mine, Mercur district, Utah, gave (anal. by W. F. Hillebrand) :

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	SrO.	MgO.	$(K,Na)_2O$.	As_2O_5.
7·08	26·46	0·64	10·29	2·10	trace	0 12	33·82

P_2O_5.	SO_3.	CO_2.	F.	Cl.	H_2O.	Total.
0·94	0·27	0·88	0·21	trace	17 23	100·04

Of the water, 3 22% is lost at 110°, and the remainder below redness. Deducting silica, strontianite, and gypsum, these results correspond with $3(AlO_2H_2)_3AsO_4,3H_2O + Ca_3(AsO_4)_2$, or with

$$Ca_3(AlO_2H_2)_5(AsO_4)_3,5H_2O.$$

Whether the substance is to be regarded as a simple mineral or as a mixture of liskeardite $[(AlO_2H_2)_3AsO_4,5H_2O]$ and berzeliite $[Ca_3(AsO_4)_2]$ is left undecided.   L. J. S.

Preslite [= Tsumebite], a New Mineral from Tsumeb, German South-West Africa. VOJTĚCH ROSICKÝ (*Zeitsch. Kryst. Min.*, 1912, 51, 521—526).—The mineral was observed in small, emerald-green crystals associated with chessylite, cerussite, calamine, and dolomite. The crystals are imperfectly developed, and appear to be orthorhombic $(a:b:c = 0·977:1:0·879)$ with complex twinning ; D 6·09, $H = 3\frac{1}{2}$. A partial analysis by J. Frejka gave :

PbO.	CuO.	P_2O_5.	H_2O.
65·09	11·97	10·26	not det.

In a postscript it is admitted that this mineral is identical with the recently-described tsumebite of K. Busz (this vol., ii, 65).   L. J. S.

Chemical Composition of the Haüynite of the Albanian Hills. NICOLA PARRAVANO (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 631—633).—The mineral has the following composition :

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	SO_3.	Cl.	Total.
32·18	27·11	10·26	16·34	0·08	14·10	0·31	100·31

The total being arrived at by deducting 0·07 for oxygen replaced by chlorine. This analysis agrees with the formula suggested by Brögger and Bäckström (A., 1891, 25).   R. V. S.

Alunogen and Halotrichite. JOHANNES UHLIG (*Centr. Min.*, 1912, 723—731, 766—776).—A review is given of the literature of these

minerals, and the following formulæ are considered as the most probable : alunogen, $Al_2S_3O_{12},16H_2O$; halotrichite, $FeAl_2S_4O_{16},24H_2O$. A sample of "hair-salt" from a cave in the Waitopu valley in the Rotorua volcanic district, New Zealand, is yellowish-white and finely fibrous. Under the microscope it is seen to consist of a mixture of fibres of halotrichite (with oblique extinction of 38°, and $n = 1·49$) and scales of alunogen ($n = 1·47$). D 1·735—1·899. The following analysis corresponds with 48·30% alunogen, 41·98 halotrichite, with a little free sulphuric acid, etc. The material is soluble in water, and the insoluble residue consists of 0·70 sulphur, 4·15 silicates.

Al_2O_3.	Fe_2O_3.	FeO.	Na_2O.	K_2O.	SO_3.	H_2O.	Insol.	Total.
11·59	1·24	3·26	0·86	0·53	35·43	42·43	4·85	100·19

Microscopical examination of similar materials from other localities shows the frequent intermixture of alunogen and halotrichite, together often with some gypsum.   L. J. S.

Analysis of Garnet from Tavolato. G. SIROVICH (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 643—645 *).—Two garnets analysed had the following compositions, respectively :

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Na_2O.	H_2O.	Total.
I.	36·74	1·04	5·23	21·10	2·21	31·65	0·96	0·38	0·10	99·41
II.	37·88	0·96	5·46	21·13	2·17	31·02	0·84	0·29	0·08	99·83

These correspond with the accepted formula for the composition of this mineral.   R. V. S.

Kragerite, a Rutile-bearing Rock from Krageroe, Norway. THOMAS L. WATSON (*Amer. J. Sci.*, 1912, [iv], 34, 509—514).—This is a medium-grained rock of light colour and granitic texture, consisting mainly of felspar (albite-oligoclase, with some microcline and ortho-clase), much rutile, some quartz, and a little ilmenite. It is a rutile-bearing aplite, and was named kragerite by W. C. Brögger in 1904. Analysis I, by J. W. Watson, is of the rock, and II, by W. M. Thornton, of the rutile, D 2·225, isolated from it :

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.	H_2O.	P_2O_5.	S.	Total.
I.	50·52	25·00	13·98	0·49	0·16	0·34	1·05	6·18	1·00	0·50	trace	0·12	99·34
II.*	1·06	97·68	—	—	0·81	—	—	—	—	—	—	—	—100·49

* Also Cr_2O_3, 0·39 ; V_2O_3, 0·55.

L. J. S.

Analytical Chemistry.

Extraction Apparatus. HENRY J. CARY-CURR (*J. Ind. Eng. Chem.*, 1912, 4, 535).—This apparatus consists of a short metallic spiral-tube reflux condenser, the inlet and outlet tubes of which project through a metal plate which serves the double purpose of a support for

* and *Gazzetta*, 1913, 43, i, 36—38.

the condenser and a closure for the glass extraction flask. The flask is of somewhat conical form, with a long neck and flat bottom. A porcelain Gooch crucible is suspended from the condenser (in the neck of the flask) by means of platinum wire fastened into two holes bored on opposite sides of its upper rim, and in it is placed the material to be extracted. The whole apparatus is only six inches high and three inches wide.
　　　　　　　　　　　　　　　　　　　　　F. M. G. M:

Alundum not Constant in Weight. E. B. FORBES (*J. Ind. Eng. Chem.*, 1912, **4**, 544—545).—It is found that the porous earthenware material "alundum" in use for extraction vessels does not remain of constant weight when heated in contact with water; one of its constituents combines with water, forming a compound which is stable at 160°, but destroyed at considerably below 1000°, whilst a second factor, which results in a gain of weight, is also present.
　　　　　　　　　　　　　　　　　　　　　F. M. G. M.

A Modification of the Frary Electrodynamic Stirring Device. J. M. KNOTE and W. R. WORKE (*J. Ind. Eng. Chem.*, 1912, **4**, 534).—The use of a solenoid in the rapid electrolytic estimation of metals has been proposed by Frary (A., 1908, ii, 68), and the essential improvement now described consists in putting the coil of the solenoid round an iron core, covering the top with a suitable material, and placing the beaker containing the electrolyte on it; whilst the use of electrodes with bent stems fastened to a block which can be raised facilitates inspection during the course of the reaction.
　　　　　　　　　　　　　　　　　　　　　F. M. G. M.

Apparatus for Testing Water by Measurement of its Electrical Conductivity. LEONARD ARCHBUTT (*Analyst.* 1912, **37**, 538—542).—The apparatus described is known as the Digby and Biggs' "Dionic" water-tester, and its usefulness depends on the fact that the conductivity of pure water is extremely small, whilst the presence of any salt, acid, or base, in solution at once increases the conductivity. The water to be tested is filled into a U-tube, the two electrodes being fitted into the tops of the two limbs respectively. The current is supplied by a hand-driven dynamo provided with a constant-speed friction clutch which maintains a constant $E.M.F.$ of 100 volts. The current passing through the water is measured by a direct-reading conductivity meter. Boiled distilled water shows a conductivity of about 1·5; distilled water saturated with carbon dioxide, 44; Glasgow (Loch Katrine) water, 34; spring water of 18·4 hardness, 552. The standard temperature of testing is 20°. The author gives results of many experiments, and mentions instances where the apparatus would be of practical use.　　　　W. P. S.

Colour Reactions of Hydrogen. JOSÉ GIRAL PEREIRA (*Anal. Fis. Quim.*, 1912, **10**, 370—381).—Hydrogen gas, rapidly at 80°, more slowly in the cold, produces a blue coloration on passing into 2 c.c. of saturated phosphomolybdic acid, 1 c.c. of 1% palladium chloride, and 3 c.c. of water. In the cold the reaction is slower. With 2 c.c. of

10% sodium tungstate, 2 c.c. of glacial acetic acid, and 2 drops of palladium chloride, a blue colour is given similarly, and in both cases finely divided palladium is separated.

The presence of much free strong acid, the use of a saturated solution of phosphomolybdic acid, or the addition of too large a proportion of palladium all retard or reduce the intensity of the reaction.

Carbon monoxide reduces less readily and does not give a pure blue coloration.
G. D. L.

Use of Selenic Acid in the Estimation of Bromine Associated with Chlorine in Haloid Salts. FRANK A. GOOCH and PHILIP L. BLUMENTHAL (*Amer. J. Sci.*, 1913, [iv], 35, 54—62).—About 0·07 gram of the mixed salt is distilled in an atmosphere of carbon dioxide with 30 c.c. of water and 5 c.c. of 40% selenic acid, or a mixture of 1·8 grams of sodium selenate and 3 c.c. of dilute sulphuric acid (1:1). The vapours are conducted into a relay flask containing 2·5 c.c. of selenic acid and 10—15 c.c. of water, or 0·2—0·3 gram of the selenate and 1—2 c.c. of the dilute sulphuric acid; this flask is placed in an oil-bath heated at 110—115°. The vapour is then absorbed in a special receiver containing 4 grams of potassium iodide dissolved in 250 c.c. of slightly acid water and surrounded by cold water.

When the liquid in the distilling flask has boiled down to about 10—15 c.c., the boiling is stopped, and a moderately strong current of carbon dioxide passed to prevent regurgitation.

The iodine liberated by the bromine set free is then titrated as usual.
L. de K.

Preparation of Selenic Acid and Sodium Selenate Used in the Estimation of Bromine in Haloid Salts. PHILIP LEE BLUMENTHAL (*Amer. J. Sci.*, 1913, [iv], 35, 93—96).—Selenic acid is best prepared by oxidising selenium dioxide with nitric acid and potassium bromate. After the bromine liberated has been completely expelled, the solution is made slightly ammoniacal, and precipitated at boiling heat with barium chloride. The precipitate when heated with a calculated amount of sulphuric acid yields selenic acid. Sodium selenate may be prepared by mixing 1 part of selenium with 5 parts of sodium peroxide, and heating this, by degrees, in a nickel crucible. The mass is dissolved in water, evaporated to a pasty condition, and most of the sodium hydroxide removed by extraction with alcohol. The residue, consisting of sodium selenate and carbonate, is dissolved in water and carefully neutralised with sulphuric acid; on evaporation, sodium sulphate crystallises first, then a mixture of this with sodium selenate, which after being dried at 108° is then tested as to its true selenate content.

The salt may also be prepared by fusing barium selenate with an insufficiency of sodium carbonate and recrystallising the product from water.
L. DE K.

Oxygen in Brass. THOMAS TURNER (*J. Inst. Metals*, 1912, 8, 248—257).—It is not possible to estimate oxygen accurately in brass by heating in a current of hydrogen. Some zinc is always reduced, volatilised, and again oxidised at a lower temperature by the water

vapour, which thus does not reach the drying tube. This effect is also observed when hydrogen is passed over zinc oxide at 1000°.

C. H. D.

Comparison of Some Methods for the Estimation of Sulphur in Vulcanised Caoutchouc, with Especial Reference to Electrolytic Oxidation. DAVID SPENCE and J. YOUNG (*J. Ind. Eng. Chem.*, 1912, **4**, 413—416).—As a result of the comparison of numerous methods for estimating combined sulphur in caoutchouc with a standard Carius method, a modification of the electrolytic oxidation method introduced by Gasparini (A., 1907, ii, 650) is advocated as being exceedingly accurate, simple, and rapid.

About 0·5 gram of the sample in a 200 c.c. beaker is covered with nitric acid (D 1·4), and gently warmed until solution is complete; about 30 c.c. of nitric acid (D 1·5) are added, and a current of about 3 amperes with a potential of 6—8 volts passed through the solution between electrodes of platinum foil until oxidation is complete (one to four hours).

A diagram of the electrical connexions is given, and the further simplification by introducing a subsequent volumetric process (Pennock and Morton, A., 1904, ii, 206) for estimating the sulphur is discussed in the original. F. M. G. M.

Estimation of Sulphurous Acid in Sugar Cane and Beetroot Products. HENRI PELLET (*Bull. Assoc. chim. Sucr. Dist.*, 1912, **30**, 337—338).—The apparatus described for the estimation of sulphurous acid in sugar products consists essentially of a cylinder bearing marks which indicate the quantity of sugar solution to be taken for the estimation, the volume of acid, etc., to be added for neutralisation, the quantity of indicator, and the volume of standard iodine solution required to oxidise the sulphurous acid. W. P. S.

Estimation of Nitrites in Water. MAURICE DUYK (*Ann. Chim. anal.*, 1912, **17**, 445—447).—One hundred c.c. of the water are acidified with 20 c.c. of 10% hydrochloric acid, 4 grams of potassium hydrogen carbonate are added in small quantities at a time, a crystal of potassium iodide is then introduced, and, after the further addition of 1 gram of potassium hydrogen carbonate, the liberated iodine is titrated with thiosulphate solution. The addition of the potassium hydrogen carbonate is for the purpose of expelling air from the water and vessel in which the experiment is carried out; the liberated nitric oxide is also expelled, and there is, therefore, no risk of the latter combining with oxygen and reacting further with the potassium iodide. W. P. S.

Detection of Nitric Acid in Presence of Nitrous Acid. V. N. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1772—1775*).—As little as 0·0001 gram of nitric acid may be detected in presence of one hundred times as much nitrous acid by the blue coloration which it yields with a quadrivalent iridium compound. The reagent may be prepared conveniently from 0·025 gram of iridium in the form of

* and *Chem. Zeit.*, 1913, **37**, 157.

iridichloride or dioxide, which is dissolved in 3—5 c.c. of water, 100 c.c. of concentrated sulphuric acid (98—99%) being then added to the solution with constant stirring. The liquid is heated to boiling to decolorise it, and when cold is stored in a well-stoppered bottle. It should contain 96—96·5% of sulphuric acid.

To make a test, 5 c.c. of the reagent are heated to incipient boiling, and the substance to be tested, which must be in the solid state, quickly added. If, for example, a water is to be examined, it is first evaporated to dryness with a slight excess of alkali. The test-tube is not heated while the substance is being added, owing to the danger of converting the nitrous acid into nitric acid; on the other hand, if the reagent is insufficiently heated, a yellow and not a blue coloration is obtained.

With a large amount of nitrous acid, a coloration may appear after a time as a result of the reaction between nitrogen peroxide and water-vapour: $N_2O_4 + H_2O = HNO_3 + HNO_2$. By means of a tube fitted with a ground stopper and with two side-tubes for the passage of a current of carbon dioxide, the gas formed is rapidly removed and satisfactory results are obtained.   T. H. P.

Analysis of Mixtures of Nitric Acid, Carbamide, and Water. A. MASSINK (*Chem. Werkblad*, 1912, 9, 1000—1002).—To estimate nitric acid in presence of carbamide, the author titrates with potassium hydroxide and methyl-orange. The carbamide is estimated by evaporating the neutralised liquid to dryness, removing the last traces of water by repeated evaporation with 96% alcohol, and weighing the residual carbamide and potassium nitrate. The amount of nitrate present in the mixture is calculated from the volume of alkali employed in the titration. The method is rapid and accurate.

A. J. W.

Detection and Estimation of Free White Phosphorus in Phosphorus Sesquisulphide. THEOPHILE SCHLŒSING, jun. (*Compt. rend.*, 1912, 155, 1461—1464).—The phosphorus sesquisulphide is shaken for several minutes with sufficient light petroleum (b. p. <45°) to dissolve any free phosphorus present, the liquid quickly filtered, and an aliquot portion taken and quickly evaporated in a vacuum at 15—20°. The residue is oxidised with nitric acid, and the sulphur and phosphorus estimated according to Berger's method (compare A., 1907, ii, 129). In order simply to detect the presence of phosphorus, the residue, after evaporating off the petroleum, is shaken with some fine sand in a flask in the dark and carefully examined for any phosphorescent glow, which is given by minute traces of free phosphorus.   W. G.

Reduction of Manganese Dioxide by Nitrous Acid. Application of this Reaction in the Estimation of Phosphorus in Iron and Steel without Separation of Silicon. EUGEN R. E. MÜLLER (*Chem. Zeit.*, 1912, 36, 1490).—A slight modification of the author's process described previously (A., 1911, ii, 1132).

Instead of reducing the manganese dioxide formed by means of sodium peroxide, 0·5 c.c. of absolute alcohol and 1 c.c. of 10% sodium

nitrite are added, which causes the liquid rapidly to clear. After adding 1 c.c. of ammonia and boiling for a short time, the solution is ready for the molybdate precipitation.　　　　　　L. DE K.

The Estimation of Phosphorus in Lecithin. PAUL FREUNDLER (*Bull. Soc. chim.*, 1912, [iv], 11, 1041—1043).—Two to three grams of lecithin are heated with 50 c.c. of fuming nitric acid in a 500 c.c. flask on a water-bath. After two to three hours the reaction stops; 25—30 c.c. of water are then added, and 25—35 grams of finely powdered permanganate in portions of one gram at a time. When the oxidation is complete, the solution is diluted to 150—200 c.c., the manganese dioxide dissolved with sodium nitrite, and the whole evaporated to a syrup to expel the excess of acid. The phosphorus is then precipitated, without it being necessary to filter the liquid, with ammonium molybdate in the presence of ammonium nitrate, and estimated in the usual way. The method is accurate and preferable to that described by Bordas (A., 1902, ii, 587).　　　　T. S. P.

Accurate Volumetric Estimation of Phosphoric Acid in Phosphate Rock. JOHN G. FAIRCHILD (*J. Ind. Eng. Chem.*, 1912, 4, 520—522).—A modification of Pemberton's (*Pharm. Zentr.-h.*, 1911, 50, 1288) method of estimating phosphoric acid by titration with alkali hydroxide in which Sutton's (*Volumetric Analysis*) suggestion of first precipitating the phosphoric acid with barium chloride is carried out. This method is claimed to be accurate and very rapid, as, after allowing twenty minutes for the solution of the rock, about one hour is needed to finish the experiment.　　　　　F. M. G. M.

Use of "Activated" Aluminium in the Detection of Arsenic. ÉMILE KOHN-ABREST (*Ann. Falsif.*, 1912, 5, 384—388. Compare A., 1912, ii, 768).—The hydrogen required in the Marsh test for the detection of arsenic may be obtained by the action of water on activated aluminium foil, and the following method of carrying out the test is recommended: Four grams of aluminium foil in small pieces are cleaned with nitric acid, and then immersed for three or four minutes in 25 c.c. of a 1% mercuric chloride solution. The pieces of foil are now washed with water and introduced, together with 220 c.c. of water, into the flask of the Marsh apparatus. At the end of about two hours, the solution to be tested for arsenic is added; the latter solution should be neutral in reaction and measure about 20 c.c.　　　　　W. P. S.

Detection and Estimation of Arsenic in the Earth of a Cemetery. GINO ZUCCÀRI (*Gazzetta*, 1912, 42, ii, 633—638).—In view of the fact that in cases of suspected poisoning it has been suggested that arsenic may have reached a corpse from the soil of the cemetery in which it was buried, the author has made experiments on the soil of a cemetery known to contain arsenic. From samples of the soil, extracts were made with water, aqueous ammonia (1%), aqueous sodium carbonate (1%), and sulphuric acid. In all these extracts small quantities of arsenic could be detected by Bressanin's method (*Atti R.*

Ist. Ven. S. L. A., 1911, '70, 951), the organic matter being previously removed by Breteau's method (A., 1911, ii, 226).   R. V. S.

Estimation of Arsenic in Pyrites. E. SCHÜRMANN and WILHELM BÖTTCNER (*Chem. Zeit.*, 1913, 37, 19—51).—Three grams of the sample are heated in a reflux apparatus with 12 grams of chromic acid and 30 c.c. of dilute sulphuric acid (1 : 1) for four hours at boiling heat. When cold, 50 c.c. of water are added, and then 1·1 gram of cuprous chloride. After further addition of two grams of potassium bromide and 100 c.c. of fuming hydrochloric acid, the arsenic is distilled off in a current of hydrogen chloride and collected in an Erlenmeyer flask containing 150 c.c. of water and cooled by means of ice and salt. When two-thirds of the liquid has distilled over, the arsenic has generally passed over completely. This reduction with cuprous chloride is preferable to the use of sulphur dioxide.

The arsenic is now precipitated as sulphide by means of hydrogen sulphide. This is then converted in the usual manner into silver arsenate. To effect complete precipitation, the authors add a little ammonium acetate so as to remove free nitric acid, or the sulphide may be converted into arsenious acid, which is then titrated with iodine.   L. DE K.

Phenolphthalein as a Double Indicator in the Estimation of Carbon in Castings, Steel, and Alloys by Direct Combustion. P. BRÈS (*Mon. Sci.*, 1912, [v], 2, 501—502).—The carbon dioxide obtained in the ordinary combustion process is absorbed in a U-tube, one limb of which is filled with a mixture consisting of soda-lime, 80 grams, sawdust, 20 grams, potassium hydroxide solution, D 1·18, 20 c.c., and phenolphthalein, 0·3 gram. This mixture is colourless, but a red coloration develops as the carbon dioxide is absorbed by the soda-lime, and the course of the absorption may thus be observed. The other limb of the U-tube is filled with calcium chloride to prevent loss of moisture from the first limb. Any escape of unabsorbed carbon dioxide may be detected by subsequently passing the gases through a solution containing 1 part per 100,000 of potassium hydroxide and a small quantity of phenolphthalein ; 10 c.c. of this solution are decolorised by as little as 0·0002 gram of carbon dioxide.

W. P. S.

Phenolphthalein as an Indicator of the Presence of Sodium Carbonate in Sodium Hydrogen Carbonate. R. RICHTER. (*Pharm. Zeit.*, 1912, 57, 998—999).—According to the author, phenolphthalein is an untrustworthy indicator for the detection of sodium carbonate in sodium hydrogen carbonate, as the latter itself exhibits an alkaline reaction when the indicator is concentrated. At the same time, the presence of less than 4% of the normal carbonate in the hydrogen carbonate does not produce a pink coloration when the solution of the salt is treated with a small quantity of phenolphthalein (0·2 c.c. of a 0·05% solution).   W. P. S.

The Use of Potassium Palmitate in Water Analysis. CARL J. BLACHER, P. GRÜNBERG, and M. KISSA (*Chem. Zeit.*, 1913, 37, 56—58). —When potassium stearate is used in water analysis (compare Blacher and Jacoby, A., 1908, ii, 897), certain side reactions occur which are objectionable. The authors consequently recommend the use of potassium palmitate, and give the following directions for determining the temporary and permanent hardness of water. The carbonates are first titrated with $N/10$-hydrochloric acid, using dimethylaminoazobenzene as indicator, the carbon dioxide being removed by a current of air. The slight excess of acid is then neutralised with $N/10$-alcoholic potassium hydroxide, using phenolphthalein as indicator, and the total hardness is determined by titrating with $N/10$-potassium palmitate until the liquid turns decidedly red. When the water contains salts of weak acids, the neutral points of the two indicators are divergent, and the number of c.c. of alcoholic potassium hydroxide used give a measure of the content of the water with respect to these weak acids.

The estimations of sulphates and magnesium are carried out in a manner similar to that described for potassium stearate (*loc. cit.*).

T. S. P.

Quantitative Separation of Calcium and Strontium. RAMÓN LLORD Y GAMBOA (*Anal. Fis. Quim.*, 1912, 10, 389—394).—In the author's experience the indirect method of estimation by precipitation of the oxalates, conversion into carbonates, and determination of carbonic anhydride, yields more accurate results than either of the direct separations, by means of the nitrates with ether-alcohol or by means of ammonium sulphate.

G. D. L.

Qualitative Separation of Barium, Strontium, and Calcium. J. L. M. VAN DER HORN VAN DEN BOS (*Chem. Weekblad*, 1912, 9, 1002—1003. Compare *ibid.*, 5).—To detect barium, strontium, and calcium, the mixed carbonates are dissolved in dilute acetic acid, the solution boiled to expel carbon dioxide, and diluted with water. Ammonium acetate is added, any precipitate formed being filtered off, and the barium precipitated quantitatively by addition of ammonium dichromate to the boiling solution. The cold filtrate is made slightly ammoniacal, and the strontium chromate precipitated by addition of 96% alcohol. The presence of calcium in the filtrate can be detected by addition of ammonium oxalate. The method is rapid and accurate, and can also be applied to the quantitative separation of the metals.

A. J. W.

Estimation of Lead in Tin. L. VANNIER (*Ann. Falsif.*, 1912, 5, 477—478).—For the estimation of small quantities of lead in tin it is recommended that exactly 1 gram of the metal be dissolved in nitric acid, and the metastannic acid separated in the usual way. The filtrate from the metastannic acid is then diluted to 200 c.c., and 20 c.c. of this solution are treated with 1 c.c. of a 40% potassium iodide solution. If less than 0·5% of lead is present in the metal, the mixture will remain clear; 0·6% of lead will cause a precipitate of lead iodide to separate within five minutes, whilst 0·8% yields a

large quantity of precipitate. The quantity of lead may be estimated by comparison with solutions containing known amounts of lead.

W. P. S.

Use of Meyer's Reagent. UMBERTO PAZIENTI (*Boll. chim. farm.*, 1912, 51, 661—666).—The author confirms the statement of Tixier (*Bull. sci. pharm.*, 1910, 82), that the oxidation of phenolphthalin to phenolphthalein (which is the basis of the action of this reagent) is shown by water containing very slight traces of copper (one part in one million), but the reaction is entirely prevented by the addition of 0·001 gram-mol. of hydrogen cyanide. The author suggests a possible mechanism for the reaction with copper salts, which is apparently an example of catalysis involving the formation of intermediate substances. The sensitiveness of the reagent towards copper salts depends on circumstances: 0·01—0·001% of copper sulphate causes almost instantaneous oxidation of the phenolphthalin without the intervention of hydrogen peroxide, whilst when the solutions contain 0·0001— 0·00001%, the oxidation is very slow unless hydrogen peroxide is added. The maximum dilution at which copper can be detected with the reagent (hydrogen peroxide being also added) is 0·000001%, and it is thus much more sensitive than other tests for copper. Manganese, cobalt, lead, iron, platinum, and various inorganic and organic compounds also affect the reagent, which was originally suggested as a test for blood. Discussing its value for the last-named purpose, the author is of opinion that it may be used to detect blood in urine, if the latter is first "defæcated" to remove any substances which might interfere with it.   R. V. S.

A Case of Mercurial Poisoning, and the Estimation of Mercury in Textile Materials. LORENZO L. LLOYD and WALTER M. GARDNER (*J. Soc. Chem. Ind.*, 1912, 31, 1109—1111).—Cases of mercurial poisoning having occurred recently amongst the operatives in a hat factory, the authors have investigated the matter and record the results obtained. The source of the mercury was not far to seek, since the great bulk of the rabbit and other fur constituting the raw material used in the manufacture of hats is treated with an acid solution of mercuric nitrate by the fur dealers. Although much of the mercury is removed in the processes which the furs undergo, considerable quantities remain in the finished product; at the same time, portions of the mercury compounds volatilise during the operations, and the vapours may be inhaled by the workers. A hat which had been in use for about twelve months was found to contain 0·0015% of mercury. For the detection of mercury in textile materials, a portion of the latter is treated with dilute *aqua regia*, a slight excess of zinc dust is added, and the mixture is submitted to distillation with superheated steam at a temperature of 160°; the volatilised mercury is collected on a piece of copper gauze placed in the condenser. The gauze is then dried, and heated in a tube which is drawn out to a capillary, the mercury globules collecting in the latter being then identified by the iodine test. The quantity of mercury present may be estimated by extracting the material with dilute *aqua regia*, rendering

the extract slightly alkaline by the addition of sodium hydroxide, precipitating the mercury as sulphide, and then adding acetic acid. The mercury sulphide is collected on a filter, washed with water and nitric acid, and dissolved in *aqua regia*. This solution is neutralised and treated with a solution containing 0·2 gram of potassium iodide, 6 grams of sodium hydroxide, and 2 grams of ammonium chloride per 100 c.c., the coloration obtained being compared with that produced by known amounts of mercury. A kaolin filter for collecting the mercury sulphide is described. W. P. S.

Estimation of Manganese by the Bismuthate Method. HARRY F. V. LITTLE (*Analyst*, 1912, 37, 554—557).—The author records results which show that this method (compare A., 1902, ii, 107) is trustworthy in the case of both small and large amounts of manganese. The theoretical factor should be employed for calculating the quantity of manganese present, and the author prefers to dilute the oxidised solution, before titration, with an equal volume of 3% nitric acid. W. P. S.

The Estimation of Total Manganese in Soils. Ross A. GORTNER and CLAYTON O. ROST (*J. Ind. Eng. Chem.*, 1912, 4, 522—524).—It is found that the methods of Marshall (A., 1901, ii, 350) and Walters (*Chem. News*, 1901, 84, 239), as described by Washington and Hillebrand (*The Chemical Analysis of Rocks*; and *Bull.* 422, U.S. Geol. Survey) for the estimation of manganese are not applicable to Nebraska soils, and the following modification is found to give accurate results.

The soils are fused with sodium carbonate, the solution of the fused mass acidified with sulphuric acid, and oxidised with sodium bismuthate, thus converting the whole of the manganese into permanganic acid, which is then estimated colorimetrically by comparison with a standard solution of permanganic acid prepared by the reduction of potassium permanganate with sulphurous acid and subsequent re-oxidation with bismuthate. F. M. G. M.

Manganese and Phosphoric Acid Content of Honeys. ARTHUR GOTTFRIED (*Pharm. Zentr.-h.*, 1912, 53, 1440—1443. Compare A., 1911, ii, 823).—The author has determined the amount of ash, and the phosphoric acid and manganese contained therein, of a number of honeys and honey substitutes and tabulated the results. These prove that the composition of the ash of honey differs widely, and this is particularly so as regards the amounts of manganese and phosphoric acid. Whether these variations are due to the different origin of the honeys is a matter for future research. L. DE K.

Estimation of Iron in Waters. EUGENE TASSILLY (*Bull. Soc. chim.*, 1913, [iv], 13, 34—37. Compare Rosenheim and Cohn, A., 1901, i, 455 ; Oerum, A., 1904, ii, 449 ; Stokes and Cain, A., 1907, ii, 581).—The author finds that on examining solutions of ferric salts to which potassium thiocyanate has been added by Féry's spectrophotometer, (1) the absorption of light becomes constant for a definite

quantity of iron when the salts are present in the proportion

$$FeCl_3 : 11(KCNS)_3 ;$$

(2) the maximum absorption takes place in the bluish-violet, but the maximum sensitiveness is in the green, and (3) in presence of great excess of the thiocyanate the absorption, as measured by the instrument, is proportional to the amount of iron in the coloured solution.

The estimation is made by heating 100 c.c. of the water with 20 c.c. of hydrochloric acid and 0.5 to 1 gram of potassium chlorate until chlorine is no longer evolved. On cooling, 20 c.c. of thiocyanate solution (1.7%) are added, the volume is made up to 100 c.c., and the solution examined in the spectrophotometer, the percentage of iron being determined by reference to a curve prepared from data obtained by the examination of iron solutions of known strength. If a precipitate forms, this is dissolved in hydrochloric acid and added to the liquid, which is then evaporated to 100 c.c. if necessary.

<div align="right">T. A. H.</div>

Estimation of Traces of Iron in Cane and Beet Sugar Factory and Refinery Products. JOHN J. EASTICK, JAMES P. OGILVIE, and JAMES H. LINDFIELD (*Internat. Sugar J.*, 1912, 14, 428—435).—The sulphide colorimetric method described by Winkler (A., 1903, ii, 108) is recommended for the estimation of iron in sugar and sugar products. The process may be applied directly to sugar solutions or to the ash obtained from them. The standard iron solution used for comparison should be prepared from ferrous sulphate, and it has been found that if, instead of water alone, a 50% sucrose solution is employed for the preparation of this solution, the latter will keep almost indefinitely.

<div align="right">W. P. S.</div>

Rapid Estimation of Chromium in Chrome Mordants. S. JAKUBOWSKI (*Färb. Zeit.*, 1912, 23, 415—416).—The estimation of chromium can be rapidly and conveniently effected by first oxidising it to chromic acid, treating with potassium iodide, and subsequently titrating with sodium thiosulphate in acid solution.

The following oxidising agents can be employed, hydrogen or sodium peroxides or sodium percarbonate in alkaline solution. F. M. G. M.

Estimation of Stannous Chloride and of Chlorates by means of Methylene-blue. FREDERICK W. ATACK (*J. Soc Dyers*, 1913, 29, 9—10).—The process is based on the fact that, in presence of a sufficiency of free hydrochloric acid, stannous chloride has a quantitative reducing action on methylene-blue.

About 1.4 gram of the salt are dissolved up to 250 c.c. in dilute hydrochloric acid (1:1), and 25 c.c. are then titrated with $N/50$-methylene-blue (about 4 grams per litre) until the blue colour persists. This solution is checked as follows: About 0.7 gram of the pure metal is dissolved in 50 c.c. of dilute hydrochloric acid (1:1) and made up with air-free water to 250 c.c., 25 c.c. are withdrawn, 25 c.c. of hydrochloric acid are added, and titrated in a current of carbon dioxide with the methylene-blue solution. The result is not affected by the presence of antimony.

Chlorates may be estimated indirectly by this method by adding excess of stannous chloride and warming the solution in a current of carbon dioxide. When cold, an equal volume of hydrochloric acid is added, and the excess of stannous chloride titrated as directed.　　　　　　　　　　　　　　　　　　　　L. DE K.

A Volumetric Method for the Estimation of Thorium in the Presence of Other Rare Earths. The Analysis of Monazite Sand. FLOYD J. METZGER and F. W. ZONS (*J. Ind. Eng. Chem.*, 1912, 4, 493—494).—When an excess of ammonium molybdate solution is added to a cold acetic acid solution of a thorium salt, the thorium is precipitated quantitatively as molybdate. Other rare earths, such as cerium, lanthanum, neodymium, praseodymium, erbium, yttrium, and gadolinium give no precipitate under similar conditions.

The ratio of thorium to molybdenum indicates that the precipitate is a normal thorium molybdate.

As indicator, diphenylcarbazide (the solution of which must have been prepared at least two weeks previously) is employed, being used "outside" on a white tile, and at the end of the titration furnishes a pink colour which lasts about fifteen seconds and requires some experience to identify.

The analysis is carried out as follows : About 1 gram of monazite sand is treated with 10—15 c.c. of concentrated sulphuric acid in a porcelain crucible, and, after several hours' heating, carefully transferred to about 700 c.c. of cold water and left overnight; the solution is filtered, the filtrate nearly neutralised with dilute ammonium hydroxide, followed by the addition of 50 c.c. of a cold saturated solution of oxalic acid, and again left overnight.

The mixed oxalates are collected, washed with dilute oxalic acid, transferred to a beaker, and boiled with 20—25 c.c. of a concentrated solution of potassium hydroxide, diluted, the precipitate of rare earth hydroxides collected, washed, redissolved in hot dilute nitric acid, and evaporated to dryness several times with small quantities of water to remove free nitric acid. The dry residue is treated with 20 c.c. of glacial acetic acid, 300 c.c. of water and 1 gram of sodium acetate, and, when completely in solution, titrated with standard ammonium molybdate solution.　　　　　　　　　　　F. M. G. M.

Analysis of Bismuth Subnitrate. MAURICE FRANÇOIS (*J. Pharm. Chim.*, 1912, [vii], 6, 536—542; *Ann. Falsif.*, 1912, 5, 569—573).—To determine whether a sample of bismuth subnitrate contains an admixture of oxide, it is recommended that the results of analysis should be calculated into percentages of water, bismuth oxide, and nitrogen pentoxide. For the pure substance, the ratio of the percentage amounts of nitrogen pentoxide to bismuth oxide (Bi_2O_3) should be 1 to 4·296. The authors find that commercial bismuth subnitrate frequently contains less water than the quantity mentioned in the French Codex, namely, 5·8%.　　　　　　　　　　　W. P. S.

New Apparatus for the Examination of Mine Air. LEONARD A. LEVY (*J. Soc. Chem. Ind.*, 1912, 31, 1153—1155).—For

the combustion of small quantities of methane in the estimation of this gas in air, the author uses a silica capillary containing a platinum wire. The silica tube is about three inches long, and has a diameter of 1 mm., whilst the platinum wire is one inch in length, and is stretched axially in the middle of the tube; a spring at one end of the platinum wire prevents the latter from touching the sides of the tube when it is heated. The wires supplying the electric current are fused into the ends of the silica tube, and the platinum wire is heated to a white incandescence during the passage of the gas through the apparatus. The gas is admitted through a capillary side-tube near one end of the platinum wire, and a capillary side-tube near the other end is provided for the exit of the gas. Two portable forms of apparatus are described for the estimation of methane and carbon monoxide, etc., respectively, in mine air.   W. P. S.

The Estimation of Benzene in Coal Gas. ELLEN S. McCARTHY (*J. Gasbeleuchtung*, 1912, 55, 891—892).—A description of the method of estimating benzene in coal gas by means of the additive compound formed with ammoniacal nickel cyanide (compare A., 1903, i, 469).   F. M. G. M.

Estimation of Methyl Alcohol in Spirits. JOSEF HETPER (*Zeitsch. Nahr. Genussm.*, 1912, 24, 731—737).—In the method proposed, the quantity of methyl alcohol is estimated by oxidation with permanganate in phosphoric acid solution; 1 gram of methyl requires 187·5 c.c. of $N/1$-potassium permanganate solution, and 1 gram of ethyl alcohol 87 c.c. of this solution for complete oxidation. The spirit under examination is distilled, and the distilate is either diluted or concentrated by further distillation until it has D 0·910 to 0·925; between these limits, solutions of either methyl or ethyl alcohols have the same density, and the quantity of total alcohol present may be found by reference to tables. A weighed portion of about 1·5 c.c. of this alcoholic solution is then diluted to 200 c.c., and 10 c.c. are introduced into a flask containing 30 c.c. of $N/2$-permanganate solution (containing 40 grams of crystallised phosphoric acid per litre) and 60 c.c. of water. The flask is then heated on a water-bath in a reflux apparatus for two hours. After cooling, the excess of permanganate is titrated with oxalic acid solution, and the amount of methyl alcohol calculated from the quantity of permanganate reduced. The method cannot be applied to spirits containing large quantities of furfuraldehyde or ethyl acetate.   W. P. S.

The Bromine and Iodometric Methods for the Volumetric Estimation of Cresol. C. M. PENCE (*J. Ind. Eng. Chem.*, 1912, 4, 518—520).—A description of experiments from which the author draws the conclusion that the usual bromine methods for the estimation of cresols depend on certain fixed conditions, presupposing a previous knowledge on the part of the operator which renders them undesirable. Tribromo-*o*- and trihromo-*p*-cresols cannot be formed in an analogous manner to 2 : 4 : 6-trihromophenol, but *m*-cresol can be estimated by conversion into tribromo-*m*-cresol. *o*- and *p*-Cresols form

di-iodo-compounds, and this can be made the basis of a method for their estimation, but *m*-cresol does not combine quantitatively with iodine.

F. M. G. M.

The Behaviour of Blood-Sugar in Normal and Pathological Cases. I. The Technique of the Estimation of Sugar in Blood. Fr. Rolly and Fr. Oppermann (*Biochem. Zeitsch.*, 1913, 48, 50—63).—Details are given of the experimental methods for separation of the proteins, for which the dialysed iron hydroxide method of Michaelis and Rona forms the basis, and for estimation of sugar in the protein-free filtrate by Bertrand's method. S. B. S.

Analysis of Cane Molasses. Study of the Different Methods of Estimating Sucrose. C. Fribourg (*Bull. Assoc. chim. Sucr. Dist.*, 1912, 30, 312—327).—The following results were obtained by using different methods for the estimation of sucrose in a sample of molasses: Direct polarisation, after clarification with basic lead acetate, 35·90%; with normal lead acetate and calcium hypochlorite, 33·93%. Double polarisation, with basic lead acetate, 42·58%; with normal lead acetate, 41·86%. Fehling's gravimetric method, 41·44%. Double polarisation, after treatment with carhamide and hydrochloric acid, 41·52%; after treatment with sulphurous acid, 41·62%. Direct polarisation after the reducing sugars had been destroyed by means of hydrogen peroxide, 41·65%; double polarisation of this solution showed 41·57%, whilst Fehling's method yielded 41·32%. The invertase method gave 41·36%. Excluding the results obtained on solutions clarified with basic lead acetate, the average of the other figures was 41·54%. The difference between the amount of sucrose actually present and that found by the direct polarisation emphasises the necessity of employing the more trustworthy methods which are mentioned. W. P. S.

Estimation of Sugar in "Bagasse" and in Sugar Cane. Estimation of Water in "Bagasse." Henri Pellet (*Bull. Assoc. Chim. Sucr. Dist.*, 1912, 30, 305—312).—The total sugar may be estimated by treating a weighed portion of the substance with small quantities of calcium hydroxide and sodium carbonate, and extracting it with successive quantities of hot water. The solution thus obtained is clarified with basic lead acetate, and examined in the polarimeter. The small quantity of sugar which remains in the "bagasse" after this extraction is estimated in the liquid which is recovered from the moist mass by pressure. An alternative method consists in heating the "bagasse" with water in a closed vessel, and, after cooling, separating the solution by decantation and pressure; this solution is then clarified with basic lead acetate, and polarised. The method is suitable for the estimation of sugar in sugar cane provided that the latter is finely-divided previously. The moisture in "bagasse" may be estimated by heating 50 grams of the sample in a wire-gauze basket to a temperature of 110° until no further loss in weight takes place. W. P. S.

Polarimetric Estimation of Sugar in Beetroots, using the Cold and Hot Extraction Methods of Pellet. HENRI PELLET (*Bull. Assoc. chim. Sucr. Dist.*, 1912, **30**, 328—333).—Results of experiments are recorded which show that exactly the same figures are obtained, whether the beetroots are treated by the cold diffusion or by the hot digestion methods for extracting the sugar.   W. P. S.

Determination of the Polarisation of Beetroot Sugar Products by Double Polarisation. Comparison between the Carbamide-Hydrochloric Acid and Sulphurous Acid Methods. HENRI PELLET (*Bull. Assoc. chim. Sucr. Dist.*, 1912, **30**, 335—337).—The double polarisation method, using for the direct polarisation a sugar solution containing carbamide and hydrochloric acid, yields lower results than is the case when the sugar solution is treated with sulphurous acid. This is due to the action of the hydrochloric acid on the sugar. The carbamide method yields about 0·25% less sugar than the sulphurous acid method in the case of beetroot juice containing 20% of sugar, whilst with raw sugar the difference between the two methods amounts to 2·5% of sugar. A similar difference is obtained in the case of molasses, and the carbamide method cannot, therefore, be considered as trustworthy.   W. P. S.

The Gelatinising Temperature of Starch Grains. MAX NYMAN (*Zeitsch. Nahr. Genussm.*, 1912, **24**, 673—676).—Various starches were found to gelatinise at slightly different temperatures when mixed with water and heated gradually, for instance, rye starch gelatinised at 57°, barley starch at 58°, and wheat starch at 59°. The gelatinising point was taken as being the temperature at which the starch grains ceased to polarise light when examined under the micropolariscope. The larger starch grains gelatinised more quickly than the smaller. It was also found that the starches gelatinised at different rates when maintained at a temperature a few degrees below the actual gelatinising point. At 53°, rye starch is gelatinised completely in six minutes, whilst wheat starch requires twenty-four minutes. This difference may afford some slight means of identifying these two starches in mixtures of the same, as any ungelatinised grains remaining after about seven minutes' heating at 53° would indicate the presence of wheat starch.   W. P. S.

New Method of Estimating Glycogen in the Liver. HENRI BIERRY and (Mme.) Z. GATIN-GRUZEWSKA (*Compt. rend.*, 1912, **155**, 1559—1561).—A rapid method of estimating glycogen in liver. Twenty-five grams of the liver are crushed and heated to solution on a water-bath with 25 c.c. of 35% aqueous potassium hydroxide. The solution is then heated in an autoclave at 120° for half an hour, cooled, and neutralised with hydrochloric acid. Five c.c. of hydrochloric acid (D 1·18) are added, the liquid made up to 100 c.c., and again heated in the autoclave at 120° for half an hour. After cooling, it is neutralised with sodium hydroxide, the proteins precipitated by mercuric nitrate, the solution made up to 300 c.c., filtered, and the dextrose estimated in the filtrate by Bertrand's method. The

results so obtained were, in all cases, higher than those given by
Pflüger's method, but the difference was shown not to be due to the
formation of *l*-xylose by hydrolysis of nucleo-proteins in the liver.

<div align="right">W. G.</div>

The Estimation of Cellulose in Wood and Spinning Fibres.
CHARLES F. CROSS and EDWARD J. BEVAN (*Zeitsch. Farb. Ind.*, 1912,
11, 237—238).—Polemical, a further reply to König and Hühn
(A., 1912, ii, 1105).

<div align="right">F. M. G. M.</div>

Detection of Formic Acid in Fruit Products. F. L. SHANNON
(*J. Ind. Eng. Chem.*, 1912 4, 526—528).—The formic acid is isolated
by steam distillation, the volume of liquid reduced by evaporation
(after neutralisation with sodium hydroxide), and the formic acid either
reduced to formaldehyde with magnesium and dilute sulphuric acid, or
converted into the lead salt which is readily identified by its crystallo-
graphic habit.

<div align="right">F. M. G. M.</div>

Estimation of Acetyl Groups. WILHELM NORMANN (*Chem.
Rev. Fett. Harz. Ind.*, 1912, 19, 205—206).—The following method
for the estimation of acetyl groups can be completed in about two
hours. Two grams of the accurately weighed fat or oil are acetylated
by boiling with 4—6 c.c. of acetic anhydride during 0·5—1 hour, and
the excess of acetic anhydride expelled by heating in a stream of
a neutral gas such as hydrogen or carbon dioxide. The acetyl groups
are then eliminated by the action of standard alcoholic potassium
hydroxide, and the excess of alkali subsequently titrated with a
standard solution of acid.

<div align="right">F. M. G. M.</div>

The Fractional Precipitation of Mixtures of Fatty Acids.
HANS KREIS and EMIL ROTH (*Chem. Zeit.*, 1913, 37, 58).—An alcoholic
solution of the mixture of fatty acids is precipitated by about one-tenth
of the theoretical quantity of lead acetate, and the acids obtained from
the precipitate by boiling with hydrochloric acid. The melting point,
refractivity, iodine value, and molecular weight of the acids can then
be determined.

The results obtained with a number of oils are given, and it is shown
that the first fraction from rape-seed oil consists mainly of erucic acid.
Arachidic acid can be obtained from a mixture of acids by one frac-
tionation, and this is made use of in testing for earth-nut oil, the
details for which are to be given later.

<div align="right">T. S. P.</div>

Estimation of Total Tartaric Acid in Wines. PHILIPPE
MALVEZIN (*Bull. Soc. chim.*, 1912, [iv], 11, 1043—1045; *Bull. Assoc.
Chim. Sucr. Dist.*, 1912, 30, 342—343).—Twenty-two c.c. of the wine
are distilled in a conical flask until 2 c.c. only remain. The flask does
not come directly into contact with the flame, but is placed about
3 cm. above a thin metal plate, which is heated directly. To the con-
tents of the flask are then added 1 c.c. of a 10% solution of potassium
bromide and 40 c.c. of a mixture of alcohol and ether in equal volumes,
in order to favour the precipitation of the tartaric acid present, either

io the free or combined state. The flask ie then immersed for fifteen to twenty minutes in a freezing mixture made from equal weights of water and ammonium nitrate. The precipitate is collected, washed several times with the ether-alcohol mixture, then dissolved in water, and titrated with $N/10$-sodium hydroxide in order to determine the amount of tartaric acid preeent.

The volatile acids and the alcohol can be determined in the 20 c.c. of distillate obtained.   T. S. P.

Estimation of Citric Acid in the Presence of Certain Other Acide. L. GOWING-SCOPES (*Analyst*, 1913, **38**, 12—19).— The reagent used ie prepared by pouring 68 c.c. of etrong nitric acid on to 51 grams of mercuric nitrate and 51 grams of manganese nitrate. One hundred c.c. of water are then added, and when all is dissolved, the solution is made up to 200 c.c. and filtered.

A quantity of the euhstance containing not more than 0·04 gram of citric acid is carefully neptralised with $N/10$-alkali, using phenolphthalein as indicator. Ten c.c. of the reagent are added, and the whole diluted to 200 c.c. The liquid is then boiled in a reflux apparatus for three hours, and the mercurial precipitate is collected on a Gooch crucible, washed with cold water, dried in the water-oven for two hours, and weighed. The weight divided by six equale citric acid.

The following acids when present do not interfere: tartaric, succinic, oxalic, benzoic, phosphoric, sulphuric and acetic acids; malic, lactic and salicylic acids, however, cause the results to be less accurate.   L. DE K.

Estimation of Salicylic Acid and Benzoic Acid in Fruit Juices, Jame, Lemonades, etc. A. VAN RAALTE (*Chem. Weekblad*, 1912, **9**, 1004—1005).—For the estimation of salicylic and benzoic acids and "saccharin" in the articlee cited, the author recommends boiling for five houre with dichloroethylene, followed by titration with decinormal alkali and phenolphthalein. After separation from the dichloroethylene, the neutralised liquid is examined for salicylic and benzoic acids. "Saccharin" can he extracted with ether from another portion of the aqueous liquid after addition of phosphoric acid.
     A. J. W.

Nuclein Metaboliem. ALFRED STEPHAN (*Chem. Zentr.*, 1912, ii, 1783; from *Apoth. Zeit.*, 1912, **27**, 816—818).—A review of the subject. A method for estimating uric acid in blood as a copper urate ie deecribed. The method for estimating uric acid in urine recommended ie a modification of Folin's.   W. D. H.

A New Colorimetric Method for the Estimation of Uric Acid in the Blood. OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1913, **13**, 469—476).—The phosphotungstic method yields positive evidence of the presence of uric acid in the blood. All previous evidence ie regarded with euspicion. Quantitatively it gives accurate results.   W. D. H.

Comparison of the Hübl and Wys Methods for Estimating the Iodine Numbers of Fats. AUGUET (*Ann. Falsf.*, 1912, 5, 459—475).—The Hübl method yields low results as compared with the Wys method when the reagent used in the former method is freshly prepared, owing to the absence of hydriodic acid. This acid forms gradually in the alcoholic iodine solution, and the solution should not be used until it is at least twenty-five days old. The same result is attained by adding 3·5 grams of hydriodic acid to each litre of the iodine solution; the reagent itself should be prepared immediately before being required for use by mixing equal volumes of the iodine and mercuric chloride solutions. If these precautions be taken, the iodine numbers obtained by the Hübl method will agree closely with those obtained by the Wys method. The results obtained by either method are not influenced by variations in temperature varying from 10° to 25°, and for most oils one hour's contact is sufficient in the case of Hübl's reagent; a much shorter time suffices with Wys' reagent. The difference in the results yielded by the two methods does not exceed 1% for oils having an iodine number below 130. In the case of linseed oil, the absorption of iodine is only complete after eighteen hours' contact with Hübl's reagent, or two hours with Wys' reagent.
W. P. S.

Relation between the Saponification, Iodine, and Refractometer Numbers of Fats and Oils. OTTO RICHTER (*Milch. Zentr.*, 1913, 42, 7—12).—It is shown that there is a definite relation between the saponification number and the refractive index of triglycerides of the stearic acid series; from trihutyrin to trimelissin, the refractive index increases by 0·001 for each increase of 28·02 (C_2H_4) in the molecular weight. In the case of unsaturated glycerides, the refractive index increases by 0·0112 for every two atoms of iodine absorbed by the glyceride molecule. Formulæ are given for calculating the refractive index, the saponification number, or the iodine number of a glyceride when the other two constants have been estimated.
W. P. S.

Detection of Earthnut Oil in Olive Oil by the Franz-Adler Test. HEINRICH LÜERS (*Zeitsch. Nahr. Genussm.*, 1912, 24, 683—684). —Samples of olive oil which contain a large proportion of myristin yield a turbidity with the Franz-Adler test (A., 1912, ii, 815), indicating the presence of earthnut oil. The turbidity is due, however, not to arachidic acid derived from the latter oil, but to the formation of a potassium hydrogen salt of myristic acid, ($KC_{14}H_{27}O_2, C_{14}H_{28}O_2$). The production and precipitation of this salt in the test may be prevented by adding 3 drops of glacial acetic acid (in addition to the prescribed quantity of dilute acetic acid) to the saponified oil.
W. P. S.

A New Colorimetric Method for the Determination of Epinephrine (Adrenaline). OTTO FOLIN, W. B. CANNON, and W. DENIS (*J. Biol. Chem.*, 1913, 13, 477—484).—Adrenaline, like uric acid, gives a colour reaction with phosphotungstic acid, and the quantitative results are almost identical with those obtained by physiological (blood-pressure) methods.
W. D. H.

Detection of Histidine. KATSUJI INOUYE (*Zeitsch. physiol. Chem.,* 1913, 83, 79—82).—Histidine in aqueous solution reacts with diazobenzenesulphonic acid in presence of excess of sodium carbonate to give a dark red coloration, which is definite in great dilution. Histidine reacts also when combined in the protein molecule. Tyrosine, however, gives a similar coloration (compare Pauly, A., 1904, i, 1068).

Benzoylhistidine still shows the coloration; dibenzoyltyrosine no longer gives it, or does benzoylhistidine when fixed in the protein molecule. It is thus possible to distinguish between free and fixed histidine.

It is necessary to allow the excess of benzoyl chloride, with which the protein or its decomposition product is treated, to decompose before adding the diazobenzenesulphonic acid. E. F. A.

Estimation of Lipoids in Blood-Serum. LÉON GRIMBERT and M. LAUDET (*Compt. rend.,* 1912, 155, 974—976).—A rapid and moderately accurate method of estimating cholesterol, phosphorus-containing lipoids, fatty acids, and neutral fats in a small sample of blood-serum.

The serum (20 c.c.) is treated with excess of alcohol, and after twelve hours' contact it is extracted with a further quantity of alcohol. The combined extract is concentrated by distillation, the residue treated with ether, and filtered, the filtrate on evaporation leaving a residue which contains the constituents to be estimated. The residue is saponified with $N/5$-alcoholic potassium hydroxide, the alcohol removed, the liquid acidified with nitric acid, and extracted with ether, the ethereal extract on evaporation giving the cholesterol and a mixture of fatty acids. In this mixture the cholesterol is estimated by Kumagawa's method (compare A., 1908, ii, 331), the acids being obtained by difference. The aqueous layer is evaporated to dryness and calcined, the residue treated with nitric acid, filtered, and the phosphorus estimated in the filtrate as ammonium phosphomolybdate according to Villier's method (compare A., 1893, ii, 438). The weight of the precipitate divided by 2·3 gives the weight of phosphorus-containing lipoids expressed as lecithin distearate. W. G.

Mett's Method for Estimating Pepsin and the Optimal Conditions of Peptic Activity. JOHANNE CHRISTIANSEN (*Biochem. Zeitsch.,* 1912, 46, 257—287).—Satisfactory results were obtained by Mett's method, when a soft coagulum of egg-white was used. With weak acids the amount digested is nearly proportional to the time. Hydrochloric acid has a deleterious action on pepsin, and on this account, when higher concentrations of acid are used, the amount digested is not proportional to the time. Schütz's law, $y^2 = kx$, where y = length of column of egg-white digested, x = the amount of pepsin, does not hold on account of the diffusion and the injurious action of acid on the ferment. For concentrations of acid between $N/10$ and $N/20$, the relation between the amount digested and quantity of pepsin can be approximately expressed by the formula $y^{2\cdot45} = kx$. The acidity for optimal activity of human pepsin is less than that of animal pepsins. S. B. S.

General and Physical Chemistry.

Refractive Index of Metals. P. A. Ross (*Jahrb. Min.*, 1912, ii, Ref. 314—316; from *Physical Review*, 1911, **33**, 549—556).—Prisms of the metals, with a refracting angle of $15.3''$, were deposited on glass by means of the cathode rays; and the refractive indices determined for red, yellow, and blue light by the methods of deviation, interference, Newton's rings, and immersion in liquids of known refractive index. The results obtained by the different methods show some variation, but they are of the same order. The following are selected as examples (for sodium-light): copper, 0.46—0.57; iron, 1.85; lead, 1.95; platinum, 1.75—1.88; silver, 0.28—0.34; zinc, 2.11; magnesium, 0.40; gold, 0.58—0.65; bismuth, 1.98; nickel, 1.88; brass, 0.66. L. J. S.

Further Remarks on a Formula for the Index of Refraction of Binary Mixtures. ARRIGO MAZZUCCHELLI (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 701—707).—The author sustains and develops his former criticism (A., 1911, ii, 781) in view of the reply of Schwers (A., 1912, ii, 1). R. V. S.

Optical Constants of Certain Metals in the Ultra-Red. K. FÖRSTERLING and VSÉVOLOD FRÉEDERICKSZ (*Ann. Physik*, 1913, [iv], **40**, 201—232).—The optical constants of silver, copper, gold, platinum, and iridium have been calculated from observations on the influence of the metals on the polarisation of the light reflected from the polished metal surfaces. These observations were made with monochromatic light of wave-length varying from $\lambda = 1000 \ \mu\mu$ to $5000 \ \mu\mu$.

According to the electro-magnetic theory, if the dielectric constant may be neglected in comparison with the conductivity, it is to be expected that the relations $\kappa = 1$ and $n = \sqrt{\sigma\tau}$ will hold good, where κ is the index of absorption, n the refractive index, σ the conductivity, and τ the period of vibration of the incident light.

It has already been shown that these relations are not satisfied in the case of ultra-violet and visible rays, and the data now obtained lead to the same result for ultra-red radiation. H. M. D.

The Spectra of Nebulæ and the Analogies to be Drawn From Them. JEAN MEUNIER (*Compt. rend.*, 1913, **156**, 391—393. Compare A., 1912, ii, 432; this vol., ii, 24).—The greater part of the nebulæ present continuous spectra, but there are some which show a number of definite lines. The author considers that these lines all coincide with definite lines in the solar spectrum, attributed to various elements, namely, hydrogen, iron, and titanium, there being thus a marked analogy between the solar spectrum and that of the nebulæ. Finally, from Watts' examination of the spectrum from the flame of a Bessemer converter, he draws the conclusion that iron and titanium can exist in flames which are absolutely

Influence of Different Gases and of Pressure and Current Strength on the First Ultra-violet Band Spectrum of Oxygen (*Ann. Physik*, 1912, [iv], **39**, 1408—1430. Compare A., 1910, ii, 913; 1911, ii, 558).—In previous papers it has been shown that the so-called water-vapour bands in the ultra-violet region are probably due to oxygen. Further observations have now been made with different gases, purified and dried with the utmost care. Some of these experiments were made ... an arc burning between platinum electrodes at atmospheric pressure, and others at pressures of less than 1 cm. of mercury, the current being also varied considerably in intensity. The gases examined were oxygen, nitrogen, air, hydrogen, and carbon dioxide.

Both at high and low pressures, the spectral observations indicate that the ultra-violet band spectrum in question is due to oxygen and not to water vapour. Pure oxygen, which has been dried for weeks in contact with phosphoric oxide, shows the band very clearly, although the conditions of the experiment preclude the possibility of interaction of the gas with traces of either hydrogen or hydrocarbons. In comparative experiments with nitrogen and hydrogen the band was not in evidence. In air and carbon dioxide, which both show the band quite clearly, its intensity increases with pressure and temperature.　　　　　　　　　　　　H. M. D.

Systems of Series in the Spectra of Zinc, Cadmium, and Mercury. JOHANNES STARK (*Ann. Physik*, 1912, [iv], **39**, 1612—1616). —The views of Paschen (A., 1911, ii, 833) relative to the existence of certain series in the mercury spectrum are adversely criticised. According to Paschen, the lines $\lambda = 2536$ and $\lambda = 4078$ belong to the same combination series. This is not in agreement with the general behaviour of the two lines. The flame spectrum of mercury shows only the former, and in the arc spectrum the relative intensities are very different. In regard to the manner in which they are resolved by a magnetic field, there is no similarity between them and the Doppler effect for the two lines in the canal-ray spectrum afford no evidence of a series relationship. On the other hand, the behaviour of $\lambda = 2536$ and $\lambda = 1848$ is similar, and it is probable that they belong to one and the same series.

The conclusion that the zinc line $\lambda = 2138$, the cadmium line $\lambda = 2288$, and the mercury line $\lambda = 1848$ are homologous is also inadmissible. It is contradictory to the rule that the wave-length of homologous lines of elements belonging to the same periodic group increases with the atomic weight, and, in the author's opinion, the line $\lambda = 1848$ should be replaced by $\lambda = 2536$. The members of this group behave quite similarly in many ways.

The nature of certain ultra-violet doublets in the zinc and cadmium spectra is also discussed.　　　　　　　H. M. D.

Uranous chloride shows the same absorption spectrum alone and after addition of carbamide, so that no additive compound is formed. The spectrum of $M/20$-uranous sulphate is figured, and also the spectrum of the same solution after addition of glycine in the proportion of 24 mols. to 1 mol. of uranium salt; the only difference observable is a slight displacement of the maxima of the bands. The spectra of the two corresponding solutions of uranous chloride (which are also reproduced) do exhibit differences, and in this case the existence of an additive compound has been shown to be probable by chemical means.   R. V. S.

Spectrographic Studies in the Triphenylmethane Group. RICHARD MEYER and OTTO FISCHER (*Ber.*, 1913, **46**, 70—84).—The hypothesis that only such quinonoid substances of the triphenyl-methane group as contain an auxochrome group in the para-position to the methane carbon atom can possess the properties of a dye (Meyer and Fischer, A., 1911, i, 723; von Baeyer, A., 1907, i, 757) is not in accord with further experiment.

Fuchsone, $CPh_2:C_6H_4:O$, in alcoholic solution gives an absorption spectrum (bands with maxima at 380 and 260 $\mu\mu$) resembling that of the salts of phenolphthalein, and a hot alcoholic solution of benz-aurin gives a similar curve (maxima 440 and 275 $\mu\mu$); the deepening in the colour of the benzaurin solution on warming is attributed to a change into the quinonoid structure, $OH \cdot C_6H_4 \cdot CPh:C_6H_4:O$, and from the similarity of the absorption of this and fuchsone it is evident that the para-hydroxyl group is not essential to selective absorption. This is confirmed by a comparison of fuchsonimonium chloride, $CPh_2:C_6H_4:NH_2Cl$ (obtained by warming fuchsonimonium carbinol hydrochloride, $OH \cdot CPh_2 \cdot C_6H_4 \cdot NH_2,HCl$, in alcoholic solution), and Döbner's violet, $NH_2 \cdot C_6H_4 \cdot CPh:C_6H_4:NH_2Cl$, each giving similar curves with three absorption bands (maxima at 440, 330, and 260 $\mu\mu$, and at 570, 400, and 300 $\mu\mu$ respectively); an alkaline solution of benzaurin gives a similar curve with maxima at 550, 375, and 290 $\mu\mu$.

The elimination of a molecule of water is not necessary to the existence of colour in a triphenylmethane compound (compare von Baeyer, *loc. cit.*; p-hydroxytriphenylmethane, di-p-hydroxytri-phenylmethane, and p-diaminotriphenylmethane hydrochloride in

alcoholic solution all exhibit an absorption band between 250 and 300 $\mu\mu$.

The alkali salts of hydroxyphenyl- and hydroxydiphenyl-phthalide give only one-sided absorption, resembling in this a colourless solution of phenolphthalein containing excess of alkali; it is possible therefore that these compounds exist in the solutions in the carbinol structure; this view is supported by the fact that the yellow solution of hydroxydiphenylphthalide is, like phenolphthalein, decolorised by excess of alkali, the colour re-appearing on warming.

Phenolphthalein and hydroxydiphenylphthalide both dissolve in concentrated sulphuric acid to coloured solutions of which the absorption curves run roughly parallel, but that of the former contains an additional point of maximum absorption (maxima at 500 and 390 $\mu\mu$ and at 470 $\mu\mu$); the former curve is quite different from that of the alkali salt of phenolphthalein.

Fluorane, $O{<}^{C_6H_4}_{C_6H_4}{>}C{<}^{C_6H_4}_{CO}{-}O$, and dithiofluoran,

$$O{<}^{C_6H_4}_{C_6H_4}{>}C{<}^{C_6H_4}_{CS}{>}S,$$
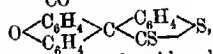
when dissolved in a mixture of acetic acid and alcohol give different types of absorption band, the former having one point of maximum absorption (at 290 $\mu\mu$) and the latter three (at 515, 360, and 300 $\mu\mu$).   D.F.T.

Spectrographic Studies in the Anthraquinone Group. RICHARD MEYER and OTTO FISCHER (*Ber.*, 1913, **46**, 85—92).—An investigation of the absorption spectra of the hydroxyanthraquinones.

The alkali salts of 1- and 2-hydroxyanthraquinone give curves which are quite different in character, the former having one large band (maximum absorption at 500 $\mu\mu$), whilst the other has three bands (maxima at 492, 300, and 238 $\mu\mu$); a neutral solution of the alkali salt of alizarin (1:2-dihydroxyanthraquinone) gives a similar absorption curve to 2-hydroxyanthraquinone (maxima at 527, 330, and 260 $\mu\mu$), but an alkaline solution gives a quite different curve (absorption maxima at 612, 560, and 266 $\mu\mu$).

The alkali salts of 1:4-dihydroxyanthraquinone (quinizarin) and 1:5-dihydroxyanthraquinone show similar absorption to 1-hydroxyanthraquinone, giving maxima at 565 and 500 $\mu\mu$ respectively; the former substance in alkaline solution gives two bands with maxima at 605 and 560 $\mu\mu$.

2:6- and 2:7-Dihydroxyanthraquinones in alkaline solution exhibit four bands, whilst 1:2:4-trihydroxyanthraquinone (purpurin), whether in excess of alkali or not, is similar to alizarin in excess of alkali.

A neutral solution of the alkali salt of 1:2:3-trihydroxyanthraquinone shows three decided bands (maxima at 510, 430, and 290 $\mu\mu$) with a much weaker one (at 620 $\mu\mu$), which develops more sharply on the addition of more alkali. The alkali salt of 5:6-dihydroxy-1:4-naphthaquinone in absorption resembles the alkaline solution of alizarin.

A comparison of these results indicates that hydroxyl in the 2-, 3-, 6-, or 7-position is more strongly auxochrome than in one of the other positions. The difference between the spectra of the alizarin and quinizarin salts in neutral and alkaline solution is probably due to the neutralisation of one hydroxyl or two, according to the conditions.

From a comparison of the above hydroxyanthraquinones with anthraquinone itself (Baly and Stewart, T., 1906, **89**, 511), all in sulphuric acid solution, the conclusion is drawn that the introduction of hydroxyl in the 2- or 3-position influences the absorption spectrum more strongly than introduction in the 1-position.

<div style="text-align: right">D. F. T.</div>

Optical Investigation of Diazo-compounds. JOHN C. CAIN (*Ber.*, 1913, **46**, 101—102).—The author draws attention to the similarity between the absorption curves of *p*-benzoquinonediazide,

and of α-naphthalenediazonium chloride, on which Hantzsch and Lifschitz (A., 1912, ii, 1116) fail to comment. The similarity must indicate an analogy of structure which is best explained by the author's diazonium formula for the latter substance (annexed formula); from the general resemblance of the curves for the above and other diazonium compounds (*loc. cit.*), the structure should be common to all.

A consideration of the author's diazonium formula would have foretold the fruitless character of certain experiments of Hantzsch and Lifschitz.

<div style="text-align: right">D. F. T.</div>

Absorption of Light and Fluorescence of Aliphatic Acid Imides (Fluorescence Phenomena among Non-aromatic Compounds. I.) HEINRICH LEY and W. FISCHER (*Ber.*, 1913, **46**, 327—335).—The authors have investigated the absorption spectra and fluorescence of imides of the general formula $R{<}^{CO}_{CO}{>}NH$, since, by suitable substitution in the group R, the substances show considerable change in colour.
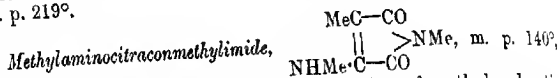
Succinimide only shows absorption at the boundary of the visible field, whilst *magnesium succinimide* is still more transparent. Dimethylmaleinimide shows distinct selective absorption. The introduction of bromine into the molecule of maleinimide has the effect of shifting the absorption towards the region of greater wave-length. The presence of an amino-group causes the absorption to shift towards the red end of the spectrum, whilst, on the addition of acid to solutions of amino-imides, the absorption is moved towards the region of shorter wave-length. In the case of amino-imides, however, it is probably that salt-formation is accompanied by inter-molecular re-arrangement.

Fluorescence of Imides.—Diphenylmaleic anhydride, diphenylmaleinimide, chloroaminomaleinimide, and methylaminocitraconic

methylimide yield fluorescent solutions when dissolved in water, alcohol, ether, or benzene, and, further, the nature of the fluorescence is found to be dependent on the particular solvent employed. Under the experimental conditions adopted, no fluorescence was observed with dimethylmaleinimide. Since, also, ethyl 5-amino-3-cyanofuran-2-carboxylate (Wislicenus, A., 1908, i, 965; Dieckmann, A., 1911, i, 457) is fluorescent, the authors are led to the

conclusion that the systems $\begin{array}{c} \cdot C-C\colon X \\ || \quad >Y \\ \cdot C-C\colon X \end{array}$ and $\begin{array}{c} \cdot C=C\cdot \\ | \quad >X \\ \cdot C=C\cdot \end{array}$ can occasion

fluorescence, if an amino-group is also present.

Chloroaminomaleinimide (compare Ciamician, A., 1890, 24) was prepared by warming dichloromaleinimide with a concentrated alcoholic solution of ammonia during two hours at 70°. It had m. p. 219°.

Methylaminocitraconmethylimide, $\begin{array}{c} \text{MeC-CO} \\ || \quad >\text{NMe, m. p. } 140°, \\ \text{NHMe}\cdot\text{C-CO} \end{array}$

was obtained by heating an alcoholic solution of methyloxalacetic ester with aqueous methylamine during three to four hours at 70°.

Diphenylmaleinimide was obtained in the form of its *copper* salt, $(C_{16}H_{10}O_2N)_2Cu$, when diphenylmaleic anhydride and copper acetate were warmed with 20% ammonia. When warmed with dilute acid, the copper salt yielded the free imide.   H. W.

Stark's Theory of Fluorescence. HANS VON LIEBIG (*Zeitsch. Elektrochem.*, 1913, **19**, 117—122).—Polemical. The author criticises Stark's statement (this vol., ii, 2) "that fluorescence is not a constitutive property of the molecule, but a property of the atom." The author, whilst admitting Stark's statement that fluorescence is due to loosened valency electrons, maintains, in opposition to Stark, that it is strictly scientific to consider the question of the relation between constitution and colour or fluorescence, only so far as the visible spectrum is concerned, and not over the whole spectrum. It is also shown that Stark's statement, based on Hartley's work, "that the colour of benzene derivatives is due only to a shift of the ultra-violet absorption bands toward the red by substitution and condensation," is not in accord with chemical facts. Stark's experiments on the fluorescence of acetone, diacetyl, etc., are held to be untrustworthy on account of the fact that such substances undergo chemical change under the influence of ultra-violet light, and that the products of such changes or the changes themselves might easily occasion the fluorescence observed. The reasons offered by Stark to explain the non-observance of fluorescence with glycerol, *p*-benzoquinone, anthraquinone, and violuric acid are regarded as insufficient to justify the statement that such substances are fluorescent. Finally, it is shown that the action attributed to the loosened valency electrons and the chromophoric groups, by Stark, is directly opposed to the main point in Stark's theory, namely, that constitution and fluorescence are entirely unconnected.   J. F. S.

The Law of Elementary Photochemical Absorption. Victor Henri and René Wurmser (*Compt. rend.*, 1913, 156, 230—233. Compare A., 1912, ii, 882, 883).—The examination of a number of photochemical reactions to see whether Grotthus's law of photochemical absorption, that the photochemical susceptibility is proportional to the absorption, holds good in all cases. For acetone and ethyl acetate the maximum decomposition corresponds with the region of maximum absorption. In the case of acetaldehyde the absorption curve presents a maximum at $\lambda = 2775$, then diminishes to a minimum, and finally increases steadily for the extreme ultraviolet rays, whilst the decomposition is a maximum at $\lambda = 2775$, and then diminishes, showing no minimum, and being very feeble in the extreme rays. In explanation of this the following law is enunciated. The photochemical susceptibility of a substance depends only on that part of the absorption spectrum which corresponds with the same molecular groupings as those on which the action is produced. W. G.

Relation between the Velocity of a Photochemical Reaction and the Incident Radiant Energy. Marcel Boll (*Compt. rend.*, 1913, 156, 138—140. Compare A., 1912, ii, 384, 407, 1119).—The author has studied the rate of hydrolysis of tetrachloroplatinic acid when submitted to rays of different energy. The light from a mercury-vapour lamp was dispersed by two quartz prisms, and certain of the resulting rays were used as a source of energy, the amount reaching the acid solution being controlled by a screen, consisting of a cell containing a dilute solution of caffeine, the concentration and thickness of the layer being varied. The coefficient of absorption of caffeine, as obtained from photometric measurements, was in close agreement with the value calculated from these results, on the hypothesis that the velocity coefficient of a chemical reaction is proportional to the incident radiant energy, even if the reaction is bimolecular. W. G.

Action of the Medium and Extreme Ultra-violet Rays on Acetaldehyde: Acidification, Polymerisation, Resinification. Daniel Berthelot and Henry Gaudechon (*Compt. rend.*, 1913, 156, 233—236).—A more detailed study of the photolysis of acetaldehyde (compare this vol., ii, 90). Initial ultra-violet rays do not convert the aldehyde into acetic acid in the absence of oxygen. Under the influence of medium and extreme rays oxidation takes place even in the absence of oxygen, a portion of the aldehyde being converted into acetic acid, and the amount of acid produced is far greater when the aldehyde is in the form of vapour than when it is liquid. With rays ($\lambda < 0.25\mu$) polymerisation is rapid, both para- and meta-acetaldehyde being formed. No resinification results from the action of initial ultra-violet rays, and it is only slowly produced by the medium and extreme rays. The presence of water checks polymerisation and resinification, but favours acidification, formic acid being formed in this case and in amount almost equal to that of the acetic acid. W. G.

Photo-electric Behaviour of Iron in the Active and Passive State. H. STANLEY ALLEN (*Proc. Roy. Soc.*, 1913, *A*, **88**, 70—74).—The photo-electric activity of chemically active iron is found to be much greater than that of iron which has been rendered passive by the action of concentrated nitric acid or by anodic polarisation in a dilute sulphuric acid solution. It is considered that this observation affords support for the theory which attributes passivity to the occurrence of a layer of gas at the surface of the metal. H. M. D.

Photo-electric Effect in Some Compounds. A. LL. HUGHES (*Phil. Mag.*, 1913, [vi], **25**, 332).—It has been suggested by Willows (this vol., ii, 4) that the photo-electric activity of moist zinc chloride may be connected with the fact that moist halogen salts of zinc emit large quantities of ions when heated to 300°, whereas the dry salts are inactive. In reply to this, the author points out that the procedure adopted in the photo-electric experiments was such as to ensure that the effect is a direct result of ultra-violet illumination. H. M. D.

Arc and Spark Lines (Uni- and Multi-valent Lines) in the Canal-Ray Spectra. JOHANNES STARK (*Physikal. Zeitsch.*, 1913, **14**, 102—109).—The conditions under which the so-called arc and spark lines of an element make their appearance indicate that the spark lines are due to carriers moving with much greater velocities than those possessed by the carriers which give rise to the arc lines. Both kinds of lines are found in the canal-ray spectra, and from observation of the canal-ray spectra of oxygen, nitrogen, chlorine, iodine, helium, sulphur and aluminium, it is found that the two groups of lines behave differently in regard to the Doppler effect. Photographs of the spectra show that in the case of the spark lines, the maximum intensity of the displaced line is separated from the undisplaced line by an intervening region of minimum intensity, whereas this region is not found in the case of the arc lines at the dispersion which was employed in the production of the photographs. The ratio of the intensity of the displaced line to that of the undisplaced line is, moreover, very much greater for spark lines than for arc lines. These facts seem to show that the difference in the two groups of lines is attributable to a difference in the magnitude of the electric charge carried by the ions. It is supposed that the carriers giving rise to the arc lines have a single positive charge, whereas the spark lines are due to carriers with two or more positive charges. H. M. D.

Doppler Effect of Canal Rays. HEINRICH WILSAR (*Ann. Physik*, 1912, [iv], **39**, 1251—1312).—The canal-ray spectra of hydrogen, oxygen, and nitrogen have been examined, and experiments made to determine the dependence of the velocity of the particles on the discharge potential, the magnitude of the Doppler effect, and the electric charges of the carriers. Other observations have reference to the influence of a magnetic field on the Doppler effect, the reflexion of the canal rays from a metal or glass surface, and the nature of the reflected rays.

The canal ray spectrum of hydrogen shows none of the lines belonging to the principal series, and lines belonging to the many-lined spectrum exhibit no Zeeman effect.

All the spark spectrum lines of oxygen which appear in the canal ray spectrum give rise to a Doppler effect of the same magnitude, and are presumably due to the same curve. On the other hand, no Doppler effect is obtained with the series lines of oxygen.

Certain nitrogen lines show the Doppler effect, and since the magnitude of this varies from one line to another, it is inferred that there are two or more carriers. The magnitude of the Doppler effect increases at first with the discharge potential, but not, as might be expected, in the ratio of the square root of the potential difference, the effect attaining a maximum at an applied potential which varies with the nature of the gas. In the case of hydrogen, the canal rays carry a single unit of charge, but multiple charges are carried by the oxygen and nitrogen canal ray particles.

The hydrogen canal rays are reflected to an appreciable extent at both glass and metal surfaces, and the reflected rays are found to behave quite similarly to the normal rays.

The carriers which give rise to the displaced lines in the canal-ray spectrum originate in the cathode region, where the rapid fall of potential occurs, and travel through the surrounding gas at practically constant speed. The luminous particles, to which the undisplaced lines are due, are accordingly unaffected by collision with the rapidly moving carriers in so far as the Doppler effect is concerned.

The excitation of a gas by the canal-ray particles of a second gas appears to be of a mutual character as a general rule. In the case of mercury, however, which is readily excited by the canal ray particles of other gases, this relationship does not exist, for the canal ray particles of mercury are apparently incapable of exciting the luminosity due to rapidly moving particles when they are allowed to pass through other gases.   H. M. D.

Comparison of the Spectra of Fluorescent Röntgen Radiations. J. CROSBY CHAPMAN (*Proc. Roy. Soc.*, 1913, *A*, **88**, 24—37. Compare A., 1912, ii, 316, 518).—Measurements have been made of the absorption in aluminium, copper, silver, and platinum of the characteristic radiations which are emitted by elements belonging to the K and L groups. The results indicate that any radiation characteristic of an element of group K, and having a certain penetrating power in aluminium, is absorbed by any other element to just the same extent as the radiation from an element of group L which has the same penetrating power in aluminium.

From experiments with bromine and bismuth which belong to the two different groups, it has been found that their radiations are equally transformed into corpuscular radiation, and that the corpuscles ejected by the radiations have the same ionising and penetrating power. Other observations show that the radiations of bromine and bismuth are identical in type in regard to their ionising power in different substances.

The fact that radiations from elements belonging to different groups are identical in nature shows that properties, which are dependent on electronic structure, are repeated in atoms of different elements containing different numbers of electrons. The observations may therefore be regarded as affording support for the theory that the corpuscles in the heavy atoms are arranged in bundles, the distribution of the corpuscles in each bundle being similar to the distribution in the atom of some lighter element. There is no relation between the elements of different atomic weight which emit identical radiations and the grouping of the periodic system.

<div align="right">H. M. D.</div>

Measurement of the Ionisation Potential in Different Gases. J. FRANCK and G. HERTZ (*Ber. Deut. physikal. Ges.*, 1913, **15**, 34—44).—The magnitude of the ionisation potential has been determined for a number of gases by a modification of Lenard's method (*Ann. Physik*, 1903, [iv], **8**, 149), an electrically heated wire being employed as the source of the electrons. In all cases the gases were carefully purified, and the following values obtained : helium, 20·5 ; neon, 16 ; argon, 12 ; hydrogen, 11 ; oxygen, 9 ; and nitrogen, 7·5 volts.

The data are insufficient to decide the question as to the manner in which the energy required for ionisation depends on the dimensions of the gas molecules.   H. M. D.

The Occlusion of the Products [of Disintegration] of Radium. GIOVANNI COSTANZO (*Compt. rend.*, 1913, **156**, 126—127).—A comparison of the results of introducing disks of palladium, rubber, and brass of varying thickness into an atmosphere activated by barium chloride containing radium. The results show (1) that brass obeys Curie's laws for the induced radioactivity of metals, (2) that palladium occludes the products of disintegration of radium almost to the same degree as rubber when in thin sheets, (3) that the thickness of the activated disks seems to have an influence on the occlusion, (4) that with disks under like conditions, the activity, immediately after withdrawal from the sphere of activation, is greater with palladium than with rubber. This radioactive occlusion could be used as a means of estimating radium in an activating atmosphere.

<div align="right">W. G.</div>

The Valency of the Radio-elements. GEORG VON HEVESY (*Physikal. Zeitsch.*, 1913, **14**, 49—62*).—From the theory of the diffusion of a cation in presence of a great excess of its anion, and assuming for the mobility of the cation a mean value of 55·7, from which none of the known cations widely depart, it is deduced that the diffusion coefficient of the cation is expressed by $1·25/n$ (cm.², day⁻¹), where n is the valency. A series of measurements of the diffusion coefficients, D, of several of the radioactive cations in $N/100$-hydrogen chloride has been carried out by the Graham-Stephan method, using the apparatus of Scheffer, and from these the valency of the ion is deduced. The results are expressed in the following table :
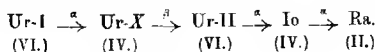
<div align="center">* and <i>Phil. Mag.</i>, 1913, [vi], 25, 390—414.</div>

Cation.	D (cm.^{2}, day^{-1}) at 18°.	Valency.	Cation.	D (cm.^{2}, day^{-1}) at 18°.	Valency.
Uranyl (UO_2'')	0·576 (in water)	II	Radium-F	0·760	II
			Thorium	0·329	IV
Uranium-X	0·400	IV	Radio-thorium	0·333	IV
Ionium........	0·327	IV	Thorium-X	0·659	II
Radium	0·667	II	Thorium-B (RaB, AcB)	1·21	I
Radium-D	0·651	II	Thorium-C (RaC, AcC)	0·625	II
Radium-E ....…...	0·646	II	Actinium-X	0·664	II

For some of these the mobility (u iu 10^5 cm., sec.$^{-1}$) has been directly determined. The value of u varies between the extremes of 54·0 for thorium-C and 68·8 for radium-F, and the more exact value of the valency, deduced by combining with u the value of D, confirm those given above. Thorium-B, which appears univalent, has a value for u 55·4, which shows that it is not an alkali metal, but is in the silver group, and is probably between mercury (univalent) and thallium in properties.

The known rule that the expulsion of an α-particle lowers the valency by two units, is, as the result of these measurements, extended and supplemented by the further rule that the expulsion of a β-particle acts in the opposite direction. After the emanation, or zero group, is reached, the opposite takes place, the change of valency with the expulsion of the positively charged α-particle always being in the direction of increasing the electro-positive character, and of the β-particle the electro-negative character. This is quite analogous to the reduction of a multivalent ion, such as the ferric or stannic ion, to the condition of lower valency, ferrous or stannous, by the loss of positive charges. The α- and β-changes have polar consequences for the residual atom.   F. S.

The **Diffusion of Uranium.** GEORG VON HEVESY and L. VON PUTNOKY (*Physikal. Zeitsch.*, 1913, **14**, 63—65*).—The diffusion of uranous and uranyl salts has been studied by chemical and radio-active methods, as if there were any difference in the rates of diffusion of uranium I and uranium II, it should be made manifest by a difference in tho two methods of measurement. In three experiments a one-fifth molar solution of uranyl nitrate in eight times molar nitric acid, the same in water, and a one-sixth molar uranous sulphate in water were diffused. The values of the diffusion coefficient D (cm.^{2}, day^{-1}) were respectively 0·442, 0·576, and 0·480, and there was in no case any difference between the results by the chemical and radioactive methods. This proves that uranium I and II diffuse at exactly the same rate. and are extremely closely allied in chemical properties. To bring the uranium disintegration scheme completely in accord with the rules as regards change of valency following α- and β-ray changes (preceding abstract), it is only necessary to assume that uranium-X is the product of uranium I, and is intermediate between it and uranium II as shown:

$$Ur\text{-}I \xrightarrow{\alpha} Ur\text{-}X \xrightarrow{\beta} Ur\text{-}II \xrightarrow{\alpha} Io \xrightarrow{\alpha} Ra.$$
$$(VI.) \qquad (IV.) \qquad (VI.) \qquad (IV.) \qquad (II.)$$

F. S.

* and *Phil. Mag.*, 1913, [vi], **25**, 415—418.

The Radioactivity of Solutions of Uranium Salts. L.
MICHIELS (*Le Radium*, 1912, **9**, 432—434).—The ionisation produced
by solutions of uranium salts of known concentration and density
has been studied by means of an electroscope with amber insulation.
These solutions lend themselves readily to the production of α-ray
standards of greater uniformity than can be produced by films of
solid uranium compounds. For a given volume and area of solution
of given density, the α-radiation is proportional to the uranium
content. If the density of a number of solutions of uranium of
different concentration is made the same by the addition of ferric
chloride, the activity is proportional to the concentration. This
allows the content of uranium in a solution to be obtained by a
radioactive method in the presence of other metals in the solution,
provided that no other radioactive material is present.   F. S.

Change in Activity of a Sample of Uranium Nitrate. M.
LA ROSA (*Nuovo Cim.*, 1913, [vi]. **5**, i, 73—82).—A sample of this salt
was found to undergo changes in radioactivity (which are described
in detail) under the influence of proximity to an electric arc, of
slight heating, or of variations in the humidity of the air with which
it was in contact. The changes observed are to be attributed to
the hygroscopic nature of the substance, and to the solubility of the
emanation which it produces in the absorbed water.   R. V. S.

Behaviour of Uranium-X with Regard to the Usual Methods
of Electrochemical Separation. PAOLO ROSSI (*Nuovo Cim.*, 1913,
[vi], **5**, i, 5—14).—The electrochemical separation of uranium-X
and uranium is more difficult than is the case with the radium
group. This would seem in agreement with Lucas's law, according
to which the radioactive elements transform themselves into electro-
chemically more noble elements, but in contradiction with this,
uranium-X is not more easily separable than uranium. When
uranium solutions are electrolysed with increasing $E.M.F.$, no
uranium-X separates at the cathode, but it may be possible to
obtain deposits at the anode which contain uranium-X and very
little uranium, if the solution contains traces of impurities, and the
deposition is probably due to these or to deposits arising from
them by electrolysis. If substances are intentionally added to the
solutions to produce anodic and cathodic deposits, the former
contain only uranium-X, whilst the cathodic deposits are inactive
or contain both uranium and uranium-X. The presence of
uranium-X in the anodic deposits cannot be explained by the
phenomenon of cataphoresis. It is more probably an adsorption
phenomenon, and this explanation is supported by the fact that
precipitates and colloidal metals acquire activity due to uranium-X
when placed in contact with uranium solutions, and the author also
finds on calculating the relative amounts of uranium and uranium-X
which should be adsorbed, that the activity of the uranium would
be masked by the much greater activity due to the uranium-X
present.   R. V. S.

Synthetic Observations on the Activity of Rain Water. José Muñoz del ·Castillo and José Barrio Fernández (*Anal. Fis. Quim.,* 1913, **11,** 89—91).—Various specimens of rain-water were shown to give in volts per litre-hour values ranging from −3·6 to 175·0.   G. D. L.

The Atmospheric Electricity and Radioactivity of the Atlantic and Pacific Oceans. I. Determination of the Emanation Content of Ocean Water. J. Laub (*Physikal. Zeitsch.,* 1913, **14,** 81—83).—A series of fifty measurements of the emanation content of the ocean water was undertaken on a voyage in the Atlantic Ocean from Montevideo through the Magellan Straits into the Pacific Ocean to Callao. The mean of all the results showed the content to be 0·1 Mache unit, the mean for the Atlantic being 0·14, for the Magellan Straits 0·09, and for the Pacific, 0·08. No dependence of the value on the place, the neighbourhood of the coast, or the temperature of the water was observed.   F. S.

Electrical Excitation in the Spraying of Liquids (Ballo-electricity). II. Christian Christiansen (*Ann. Physik,* 1913, [iv], **40,** 233—248. Compare this vol., ii, 297).—In continuation of the experiments on the electrical excitation which accompanies the spraying of liquids, observations have been made on aqueous solutions of halogen substituted fatty acids, amines, amides, esters, ∕ hydroxybenzenes, alkaloids, and certain other substances.

From the data obtained with mixed aqueous solutions it is found that solutions of two different electrolytes, which change the ballo-electrical effect exhibited by a solution of a non-electrolyte to a given extent, are also equivalent in respect of other non-electrolytes. In a similar way, solutions of non-electrolytes which are equivalent in their action towards a particular electrolyte are also equivalent in respect of other electrolytes.

The influence of the nature and the pressure of the surrounding gas on the electrical effect has also been examined. The effect increases in all cases with the pressure, and for carbon dioxide, air, coal-gas and hydrogen it increases as the density of the gas diminishes.   H. M. D.

Improved Apparatus for Measuring the Conductivity of Electrolytes. Edward W. Washburn and J. E. Bell (*J. Amer. Chem. Soc.,* 1913, **35,** 177—184).—In order to obtain an accurate method for determining the conductivity of aqueous solutions of strong electrolytes between 0·001N and 0·000001N, a study has been made of the sources of error inherent in Kohlrausch's method when applied to such solutions. Apparatus has been devised by means of which great precision can be attained, not only in the measurement of very large resistances, but also of very small ones, and which possesses the advantages of greater rapidity and convenience of manipulation. The chief modifications introduced into the usual apparatus are the substitution of a high frequency generator for the induction coil as a source of current, and of special film

resistance units for the ordinary resistance box. These resistances are made by sealing platinum wires into the ends of a glass rod and connecting them by a film of platinum deposited on the glass. A tuned telephone is employed and an extended bridge wire, all measurements being made at the middle of the bridge.

Experiments have been made with this apparatus which show that by its means the conductivity of any solution of an electrolyte from conductivity water itself up to a $6N$-solution can be readily determined with a precision of 0.01%, and that with care the precision can be increased to 0.001% in most cases. The method should prove of considerable value for the exact analytical control of pure solutions of electrolytes.   E. G.

The Molecular Conductivity and Viscosity in Mixtures of Methyl Alcohol or Acetone with Benzene and Nitrobenzene. J. FISCHLER (*Zeitsch. Elektrochem.*, 1913, 19, 126—132).—The molecular conductivity and viscosity of solutions of potassium iodide and lithium bromide were measured in solutions of mixtures of methyl alcohol and benzene, methyl alcohol and nitrobenzene, acetone and benzene, and acetone and nitrobenzene. The conductivity at infinite dilution was calculated from the results by the Kohlrausch extrapolation formula, $\lambda_\infty = (\lambda_1 \sqrt[3]{v_1} - \lambda_2 \sqrt[3]{v_2}) / (\sqrt[3]{v_1} - \sqrt[3]{v_2})$, in which λ_1 and λ_2 are the molecular conductivities at dilutions v_1 and v_2. It is shown that with lithium bromide the value λ_∞ is greater the larger the values of v_1 and v_2; the same is observed for potassium iodide, but not to so marked an extent. This irregularity is explained by the existence of complexes in the concentrated solutions which dissociate in the more dilute solutions. Walden (A., 1912, ii, 23) showed that the product $\lambda_\infty \eta$, where η is the viscosity, is a constant, and equal about 0.700. For solutions of potassium iodide in mixtures methyl alcohol–nitrobenzene, acetone–nitrobenzene, the value 0.650 is obtained, whilst the benzene mixtures give much lower values. With lithium bromide in methyl alcohol–nitrobenzene the value is low, but in the 50% acetone–50% benzene mixture it falls to 0.0487. This is no doubt due to the complexity of lithium bromide in the solution (see Serkov, A., 1909, ii, 372; 1910, ii, 177). The complexity of lithium bromide in the methyl alcohol and nitrobenzene mixtures is calculated by the Serkov formula, and it is seen to be strongly complex.   J. F. S.

Aqueous Solutions of Ammonia Soaps. I. FRANZ GOLD-SCHMIDT and LÉON WEISSMANN (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 18—31. Compare A., 1912, ii, 728).—The electrical conductivity and viscosity of solutions of an ammonia soap, prepared from the fatty acids of palm oil, has been examined in regard to the influence of concentration, temperature, and of the addition of ammonia and ammonium salts. The results are compared with those obtained in a previous investigation (*loc. cit.*) of the properties of solutions of a similarly prepared potassium soap.

The relationship between the conductivity and concentration is represented by a straight line which cuts the concentration axis

at a point on the positive side of the origin. The molecular conductivity, which is only about half as large as that of the potassium soap, increases with the concentration, and appears to approach asymptotically to a limiting constant value. The viscosity increases with the concentration at a gradually increasing rate, and the concentrated solutions are characterised by viscosity values which are extremely sensitive to changes of temperature.

The addition of ammonium chloride in small quantities increases the viscosity considerably, and causes a diminution in the conductivity. Larger quantities give rise to the precipitation of acid soaps. On addition of successive quantities of ammonia, the viscosity rises slightly at first, then falls, and finally increases until the viscosity becomes much greater than that of the pure soap solution. The effect of an addition of ammonia on the conductivity is to increase it at first, but a maximum value is soon reached, and further quantities result in a continuous fall in the conductivity.

From observations made with solutions to which both ammonium chloride and ammonia were added, it has been found that the increase in the viscosity produced by the addition of a given quantity of ammonium chloride is enormously magnified when ammonia is also present in the solution. For each concentration of ammonium chloride there is a particular ammonia concentration for which this effect has a maximum value. If this quantity of ammonia is exceeded, the viscosity falls very rapidly.   H. M. D.

Electrochemistry of Non-aqueous Solutions. X. Schützenberger's Etherobromide. VLADIMIR A. PLOTNIKOV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1919—1929).—The author challenges McIntosh's statements (T., 1905, **87**, 784 ; A., 1911, i, 256) that the electrical conductivity of Schützenberger's etherobromide (ether tribromide)(*Annalen*, 1873, **167**, 86) is due to the presence of hydrogen bromide developed in consequence of the gradual bromination of the ether, and that, in addition to the tribromide, a dibromide also exists.

As regards the first point, seven separate series of observations of the conductivity give concordant results (A., 1907, ii, 152), and the magnitude of the conductivity diminishes with lapse of time. Secondly, measurements of the viscosity of the system ether–bromine give no indication of the existence of a dibromide of the empirical formula Et_2OBr_2 (compare Kurnakov and Anisimov, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1005).

Solutions of ether dibromide in chloroform and ethyl bromide exhibit conductivities of the same order of magnitude as those of aqueous salt solutions, the specific conductivity increasing approximately in proportion to the concentration. On electrolysis, ether is liberated at the cathode, and bromine, in amount corresponding with the formation of the ion Br', at the anode. These results are in agreement with the hypothesis that the electrolytic conductivity of a solution is conditioned by the electrochemical relations of the solute with the solvent, and not by any special property, such as the dielectric constant, of the solvent.

Assuming the double formula for ether dibromide, a represen-

tation of its structure according to the co-ordination theory is
suggested.   T. H. P.

**The Apparent Potential Difference of Contact of a Metal
and Electrolytic Solutions.** J. GUYOT (*Compt. rend.*, 1913, 156,
220—222).—The author has measured the potential difference
between a gilded electrode and solutions of metallic chlorides with
an unpolarisable electrode of mercury coated with calomel, and
secondly, solutions of silver salts with a silver electrode. From his
results he deduces the following law. There exists the same
apparent potential difference between gold and equimolecular solu-
tions of electrolytes containing a common ion and having an
electrode corresponding with this ion.   W. G.

Theory of the Skinner-Case Electrolytic Thermo-element,
Sn(CrCl₃)Pt, **and on Other Elements of Analogous Type.** ROBERT
KREMANN and FELIX NOSS (*Monatsh.*, 1913, **34**, 7—67).—The *E.M.F.*
of a cell composed of tin or tin amalgam and platinum or carbon in a
dilute solution of chromic chloride increases with the temperature,
but the observations of Skinner (A., 1896, ii, 3) did not agree with
those of Case. Since the action of the cell depends on the reaction
$2CrCl_3 + Sn \rightleftharpoons SnCl_2 + 2CrCl_2$, this equilibrium has been studied at
the outset. The results show that the dissolution of the tin increases
slowly from 22° to 42°, faster from 42° to 62°, and rapidly from
62° to 80°. The constant K from the expression
$$(CrCl_3)^2 / \{(SnCl_2)(CrCl_2)^2\}$$
increases with increasing dilution, which is explained by assuming
that it is only the green variety of chromic chloride which takes
part in the reaction (compare Olie's study of the equilibrium, violet
$CrCl_3 \rightleftharpoons$ green $CrCl_3$, A., 1906, ii, 859). For the purpose of the
further investigations it was necessary to know the dependence of
the amount of tin in solution on the original concentration of the
chromium chloride and on the temperature, and therefore the
factor $SnCl_2/CrCl_2 + CrCl_3$ has been plotted against chromic chloride
(constant temperature) and temperature (constant initial concen-
tration). The stronger the solution, the faster does this factor rise
with temperature.

Measurements of *E.M.F.* under different conditions were made;
the *E.M.F.* of the system platinum or carbon as +pole, and tin or
tin amalgam as −pole, in pure chromic chloride (5 mols. per 100)
is independent of temperature, and is about 1 volt, but when the
solution is saturated with tin the *E.M.F.* falls off enormously. The
potential drop Pt|CrCl₃ is also strongly affected by changes in the
solution, from which the conclusion is drawn that the tervalent
chromium ions are reduced at the anode, a change which is very
dependent on temperature. Hence, when an exhausted cell, that
is, one which is saturated with tin and chromous chloride, is raised
to a higher temperature, more tin dissolves, the reduction of
$Cr^{\cdots}$-ions to $Cr^{\cdot\cdot}$-ions can proceed farther, and a further current
is obtained. When the element has been exhausted at a high tem-

perature (93°), no further current is developed on cooling, since a series of saturations is passed through, but when heated afresh the current is renewed. The quantity of current measured by a copper voltameter is, however, small, but it is about three times as much at 96° as at 18°. It remains constant for some time, then falls, and later on rises again, this change being accompanied by the precipitation of insoluble chromium sesquioxide.

Other equilibria have been studied, and the systems copper–chromic chloride–carbon, tin–vanadic chloride–carbon, and silver–chromic nitrate–carbon, were found to show similar electrical effects, although in the latter case the instability of chromous nitrate soon renders the silver passive, and consequently the potential difference between the electrodes smaller.   J. C. W.

The Influence of High Pressures on Faraday's First Law. ERNST COHEN (*Zeitsch. Elektrochem.*, 1913, **19**, 132—133).—The amount of silver deposited in two coulombmeters, one at atmospheric pressure, and the other at pressures of 500, 1000, and 1500 atmospheres, was compared. In most cases the weights are found to be identical; in one case there is a difference of 1 in 15,500. From the results the author draws the conclusion that the ionic charge does not vary 1 in 17,000 on changing the pressure from one atmosphere to 1500 atmospheres.   J. F. S.

Anodic Oxidation of Ammonia in an Acid Liquid in the Presence of Silver Salts. GINO SCAGLIARINI and A. CASALI (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 726—729; *Gazzetta*, 1913, **43**, i, 30—36).—When a solution of ammonium sulphate saturated with silver sulphate and contained in a porous pot is used as anodic liquid, and a solution of sulphuric acid (10%) is taken as cathodic liquid, on electrolysis some nitric acid is formed round the anode. From the authors' experiments the production of the acid appears to be favoured by rise of temperature (about 3·5 grams of nitric acid per 100 grams ammonium sulphate at 90°, as compared with 0·13 grams at 0°), but the amount of nitric acid formed is inversely proportional to the concentration of the ammonium sulphate. The production of nitric acid falls off as the experiment is continued, probably owing to migration of the catalyst from the anodic compartment.   R. V. S.

The Mechanism of the Chlorination of Benzene in the Electrolytic Cell. RALPH G. VAN NAME and CARLTON H. MARYOTT (*Amer. J. Sci.*, 1913, [iv], **35**, 153—170. Compare Cohen, Dawson, and Crossland, T., 1905, **87**, 1034).—The electrolysis of benzene in solution of lithium chloride in glacial acetic acid gives chlorinated benzenes, under favourable conditions, to the extent of 50—70% yields. Both addition and substitution products are formed, the latter predominating, but there is nothing to show that the effects are not due to the secondary action of chlorine previously set free by the current and dissolved in the electrolyte. Benzene dissolved in the same solution is readily chlorinated by direct treatment

with chlorine gas in the dark, yielding additive and substitution compounds in proportions which vary with the conditions.

The addition of benzene to the acetic acid–lithium chloride solution during electrolysis raises the anode potential by an amount equal to or greater than that produced by a similar amount of carbon tetrachloride. This indicates that benzene has little or no depolarising action towards chlorine, at least in this case, and therefore that the chlorination of the benzene is not electrolytic in character. Phenol, added under similar conditions, produces a decided lowering of the anode potential, substitution products being formed.

The rate of chlorination of benzene, when dissolved in the same medium saturated with chlorine, was measured at $10.2°$, and then the rate under simultaneous electrolysis. In the latter case there was no perceptible acceleration of the rate of chlorination under conditions where a 10% current yield should have been evident. Both additive and substitution products, in the ratio of about $2:3$, were formed, this ratio increasing with the progress of the reaction. The reaction velocity calculated on the assumption that monochlorobenzene and benzene hexachloride were the sole products, showed a steady rise, but the rate of chlorination of monochlorobenzene, as determined separately, appeared to be sufficient to account for this effect.

From the above results it follows that there is no positive evidence of strictly electrolytic, that is, anodic, chlorination of benzene.

T. S. P.

Measurement of the Energy of the Ultra-violet Radiation Emitted by an Arc in Mercury Vapour under Different Conditions. MARCEL BOLL (*Compt. rend.*, 1913, **156**, 313—315).— A study of the energy emitted by a mercury-vapour lamp under varying conditions of voltage and current strength. The results show that the energy for $\lambda = 2536$ emitted by the arc in mercury vapour is a parabolic function of the electrical power expended. A formula is given by means of which an approximate calculation can be made for the radiation from such a lamp under any conditions.   W. G.

Selective Absorption of Electromagnetic Waves. W. ROMANOV (*Ann. Physik*, 1913, [iv], **40**, 281—296).—The author has investigated the absorption of electromagnetic waves of wave-length ranging from about 40 to about 100 cm. in methyl, ethyl, *n*-butyl, and amyl alcohols. The curves which are obtained b plotting the absorption coefficient as a function of the wav length exhibit distinct maxima and minima, indicating that th absorption spectrum for long-waved electromagnetic waves is quit similar to the spectrum obtained in the case of heat rays. H. M. D.

The Additivity of Diamagnetism in Compounds. PAUL PASCAL (*Compt. rend.*, 1913, **156**, 323—325. Compare A., 1910, ii, 100, 179).—The absolute values of the atomic coefficients of mag-

netisation of a number of non-metallic elements, as calculated by difference from the coefficients of simple organic compounds containing them, the coefficient for water being taken as -7.2×10^{-7}, show a very close accord with the values obtained directly on the elements. In the case of a diamagnetic metal, the coefficient, similarly calculated by difference, is not a constant value, but diminishes with increase in molecular weight of the organo-metallic compound, the values for a homologous series tending towards a limit figure, which, for the metals studied (tin and mercury), show a striking agreement with the values obtained by direct determination. This method of difference thus affords means of determining the coefficient of magnetisation of diamagnetic elements, which it is difficult to prepare in the pure state, but of which pure organo-derivatives can be prepared. W. G.

Relative Scale of Temperature for Solid Substances. HANS ALTERTHUM (*Ber. Deut. physikal. Ges.*, 1913, **15**, 25—33).—A theoretical paper in which, in reference to the Planck-Einstein formula for the energy content of a solid substance, it is suggested that the temperature of a solid should be expressed on a scale determined by the condition that the energy content is directly proportional to the temperature. This scale will vary from one substance to another, and even in the case of substances of high melting point, the melting points on the relative scale will differ materially from those on the absolute scale. The author considers that Lindemann's formula (*Physikal. Zeitsch.*, 1910, **11**, 609) for the connexion between the melting point and the vibration frequency should be modified in such a way that the melting temperatures are expressed on the relative scale. The modified formula is applied to the data for silver, aluminium, copper, lead, platinum, and zinc. H. M. D.

Specific Heat of Helium and Certain Diatomic Gases between 20° and −180°. KARL SCHEEL and WILHELM HEUSE (*Sitzungsber. K. Akad. Wiss. Berlin*, 1913, 44—48).—The measurements were made by the method of continuous flow with the apparatus described in a previous paper (A., 1912, ii, 19). From the molecular heat at constant pressure (C_p), that at constant volume (C_v) has been calculated. The following pairs of numbers represent respectively the values of C_p and $k = C_p/C_v$: helium, 18° (4.993, 1.660), −180° (4.934, 1.673); hydrogen, 16° (6.860, 1.407), −76° (6.365, 1.453), −181° (5.330, 1.597); nitrogen, 20° (6.983, 1.400), −181° (7.162, 1.468); oxygen, 20° (6.98, 1.399), −76° (6.86, 1.416), −181° (7.30, 1.447); air, 20° (6.965, 1.401), −76° (7.04, 1.401), −181° (7.23, 1.450); carbon monoxide, 18° (7.006, 1.398), −180°, (7.244, 1.472). The above data are compared with the results of other observers, and evidence adduced which indicates that the probable error attaching to Regnault's numbers is not less than about 1%. In the case of all the diatomic gases examined, it is found that the specific heat ratio increases very considerably when the temperature is lowered from 20° to −180°.

Molecular heat values have also been calculated for the various gases on the assumption that they obey the simple gas laws.

H. M. D.

Influence of the Free Electrone on the Specific Heat of Metals and Alloys. OSKAR RICHTER (*Ann. Physik*, 1912, [iv], 39, 1590—1608).—The specific heats of complete series of bismuth–tin and bismuth–lead alloys have been determined, with the object of ascertaining whether free electrons contribute in measurable amount to the heat capacity of metals. For both series of alloys the electric and thermal conductivities are much smaller than would be expected according to the mixture rule, and in both series it has been found that the deviations from the straight line relationship are such that the ratio of thermal to electric conductivity remains constant. According to Drude's theory, the diminution in the electric and thermal conductivity observed in a binary alloy of this type is due to a decrease in the number of free electrons, and if these electrons are of any appreciable importance in connexion with the heat capacity of the alloys, it should be possible to detect corresponding deviations from the mixture law in the specific heat values.

The measurements were made in a Bunsen ice calorimeter, and control experiments indicate that the accuracy attained in the specific heats amounts to 0.01 to 0.02%. In the case of the bismuth–tin alloys the observed specific heats are slightly greater than the calculated values if the mixtures close to the tin end of the series are excepted. For the bismuth–lead series the differences between observed and calculated values are in the same direction but of much greater magnitude, a maximum difference being exhibited by the alloy containing equal weights of the two metals.

These experimental measurements afford therefore no evidence in support of the view that the free electrons are responsible for a measurable fraction of the total heat capacity of the metallic alloys. This result is quite consistent with the theory of specific heat put forward by Richarz.   H. M. D.

[Law of Dulong and Petit.] FRANZ RICHARZ (*Ann. Physik*, 1912, [iv], 39, 1617—1624).—The author discusses the relation between Einstein's theory and the views which he has put forward in reference to the law of Dulong and Petit. It is claimed that the essential difference is to be found in the special assumptions made by Einstein as to the mechanism by which energy transfer takes place between the atoms. These assumptions lead to the conclusion that the atomic heat cannot be greater than the normal value. Since this is not in agreement with experiment, it would appear that these assumptions must be modified, and it is suggested that the electrons responsible for the conductivity are also involved in the process of energy transfer. In addition to this, it would appear to be necessary, in those cases where the normal value of the atomic heat is exceeded, to assume that these electrons are responsible for a portion of the absorbed heat energy. The fact that the

strongly electro-positive alkali metals have abnormally high specific heats at moderate temperatures is regarded as distinctly favourable to this view.

A further factor which may influence the atomic heat is the formation of atomic complexes. This will reduce the degree of freedom of the vibrating atoms, and lead to a diminution in the heat capacity. This may give rise to a variation of the specific heat with the temperature, which is quite independent of that indicated by Einstein's theory.   H. M. D.

Internal Pressure in Fluids. ÉMILE H. AMAGAT (*Ann. Chim. Phys.*, 1913, [viii], **28**, 5—48).—A résumé of work already published in A., 1909, ii, 549; 1911, ii, 1061, and 1912, ii, 428.   T. A. H.

Melting Curves of Stable and Metastable Crystalline Substances. FRIEDRICH KÖRBER (*Zeitsch. physikal. Chem.*, 1913, **82**, 45—55).—From considerations of the Z-function of the thermodynamic potential, it was shown by Tammann (*Göttinger Nachr. math.-phys. Kl.*, 1911, 353) that the melting curves of the stable and metastable forms of a substance would probably not cut one another. The present paper gives an account of the determination of the melting curves of the two forms of acetamide, phthalide, ethyl aminocrotonate, chloroacetic acid, and sodium thiosulphate. These were determined at pressures from 1 to 2875 atmospheres, and although it is the opinion of the author that the pressure applied was not high enough to finally settle the question, yet the results point to the conclusion that the two curves do not cut one another.   J. F. S.

Latent Heats of Vaporisation and Maximum Pressures. ANATOLE LEDUC (*Compt. rend.*, 1913, **156**, 225—227).—Combining Clapeyron's formula for the latent heat of vaporisation with his own formula for the specific volume of the saturated vapour (compare A., 1912, ii, 831), and taking previously recorded values for the maximum pressures and specific heats of water, ether, and benzene, the author has calculated the latent heat of vaporisation of these substances at temperatures above their boiling points. His calculated results being at variance, particularly in the case of ether and benzene, with the experimental values recorded by other workers, the author suggests the advisability of redetermining the values of the maximum pressures on the pure substances, the temperatures being converted to the thermodynamic scale.   W. G.

Constancy of the Boiling Point of Sulphur. WALTHER MEISSNER (*Ann. Physik*, 1912, [iv], **39**, 1230—1242).—In utilising the boiling point of sulphur as a thermometric fixed point, the mercury or resistance thermometer is usually surrounded by a protecting cylindrical or conical sheath of some material, such as glass, asbestos, iron, or aluminium. With the object of determining the influence, if any, of the nature of the protecting sheath, comparative measurements have been made with sheaths of different

materials. These indicate that aluminium or other good reflectors cannot be satisfactorily employed in the standardisation of thermometers by means of the boiling point of sulphur, for the temperatures indicated are appreciably too low, the difference amounting to as much as $0\cdot2^\circ$. If the aluminium sheath is blackened or lined on the inside with asbestos paper, the depression, caused by the reflection from the metal surface, disappears, and the normal boiling point is recorded.   H. M. D.

The Vapour-pressure Curve of Nitrogen Tetroxide. FRANZ RUSS [with ERNST EBERWEIN] (*Zeitsch. physikal. Chem.*, 1913, **82**, 217—223).—The present paper is an account of experiments of the same nature as those of Scheffer and Treub (A., 1912, ii, 132). The experimental pressures were obtained by use of a mercury mano-meter, and despite what is said by Scheffer and Treub against the use of mercury for pressure determinations of this type, they agree very well with those obtained by means of a glass manometer. The vapour pressures were determined from -80° to -15°, and are compared with values of Guye and Drouginine (A., 1910, ii, 1056), and found to differ more and more from these values as the tem-perature is reduced. The vapour pressure is controlled by a calculation of the heat of sublimation of nitrogen tetroxide by the Clausius formula, the value 10,850 cal. being obtained. This agrees well with value of Berthelot and Ogier (*Landolt Börnstein "Tabellen"*) and Ramsay (T., 1890, **57**, 590). The pressure values are also calculated from the Nernst equation, making use of the critical pressure 100 atmospheres as deduced by Scheffer and Treub (*loc. cit.*). The calculated and experimental values agree fairly well. J. F. S.

Simple Demonstration of the Lowering of Vapour Pressure. WALTER W. REED (*Chem. News*, 1913, **107**, 64).—The lowering of the vapour pressure of a solvent by a solute at ordinary temperature is readily demonstrated by using three similar thermometers, two of which are treated as "wet bulbs" in hygrometry, the wick in one case dipping into the pure solvent, in the other case into the solution. It is found that the thermometer with the wick dipping into the solvent has a lower reading than that with the wick dipping into the solution, and that both readings are lower than that indicated by the dry-bulb thermometer. The apparatus is available for organic solvents as well as for water.   H. W.

Variation of the Vapour Pressure of Aqueous Sulphuric Acid Solutions with the Temperature. CARL HACKER (*Ann. Physik*, 1912, [iv], **39**, 1338—1349).—According to the relationship known as von Babo's Law, the ratio between the vapour pressure of an aqueous solution (p_s) and that of pure water (p_w) is inde-pendent of the temperature. This empirical result is, however, inconsistent with the requirements of thermodynamics, which leads to the relation $d(\log p_s/p_w)/dT = \Delta/RT^2$, where Δ represents the heat of dilution of the solution. In view of this discrepancy, the [author has] made measurements of the difference between the vapour

pressure of water and a number of aqueous sulphuric acid solutions at temperatures between 30° and 80°. The data show that the ratio $(p_w - p_s)/p_w$ is by no means constant, but diminishes as the temperature rises. In the case of a solution containing 32·59% of sulphuric acid, the value of this ratio was found to fall from 0·277 at 31·3° to 0·252 at 80·3°; for a solution containing 41·54% of acid, the ratio fell from 0·460 at 32·6° to 0·430 at 60·8°.

By reference to Thomsen's data for the heat of dilution of sulphuric acid solutions, it is shown that the observed variation of $(p_w - p_s)/p_w$ with the temperature is in fairly good agreement with that calculated from the above thermodynamic relation. In making this comparison, it has been assumed that the heat of dilution of sulphuric acid solutions may be regarded as independent of the temperature.   H. M. D.

Thermochemical Investigations in the Alicyclic Series. WALTER A. ROTH and GUSTAF JIM ÖSTLING (*Ber.*, 1913, **46**, 309—327. Compare T., 1912, **101**, 457; A., 1910, ii, 586; 1911, ii, 1065, etc.). —The following molecular heats of combustion at constant pressure have been determined: Methyl *cyclo*propane-1:1-dicarboxylate, 827·7 Cal.; *cyclo*propanecarboxylic acid, 479·7 Cal.; ethyl *cyclo*butanecarboxylate, 966·0 Cal.; *cyclo*butanecarboxylic acid, 641·6 Cal.; dimethyl*cyclo*butane-1:2-dicarboxylate, 984·5 Cal.; methyl *cyclo*pentane-1:2-dicarboxylate, 1117·7 Cal.; methyl α-tanacetone-dicarboxylate, 1452·9 Cal.; keto-α-tanacetonecarboxylic acid, 1328·7 Cal.; *cis*-methyl norpinate, 1288·8 Cal.; methyl pinate, 1441·6 Cal.; methyl pinonate, 1478·8 Cal.; methyl *spiro*heptanedicarboxylate, 1409·1 Cal., β-pinolene or *cyclo*fenchene, 1471·1 Cal.; cyclene, 1469·1 Cal.; thujane, 1508·6 Cal.; thujyl alcohol, 1479·4 Cal.; thujone, 1431·9 Cal.; camphor, 1412·7 Cal. The following dissociation constants in aqueous solution at 25° were also determined: *cyclo*propanecarboxylic acid, 0·0000136; keto-α-tanacetonecarboxylic acid, 0·0000115; *cyclo*butanecarboxylic acid, 0·0000173; pinonic acid, 0·0000215.

From a consideration of the above and other data, the authors come to the conclusion that Stohmann's rule, according to which the molecular heats of combustion and dissociation constants run parallel, holds very well for the simple polymethylene acids, but not for the two keto-acids, keto-α-tanacetonecarboxylic acid and pinonic acid.

The relation between ring-form and energy-content, as put forward by Stohmann-Kleber and Berthelot, is verified for the simpler compounds. The order of the energy-content is: five-ring, six-ring, double linking, three-ring, four-ring. A seven-ring appears to have a somewhat greater energy-content than a six-ring.

The influence of conjugation or non-conjugation, semi-cyclic or endo-cyclic position, of the double linking is discussed, since these secondary influences make comparison very difficult. A marked non-symmetrical structure appears to increase the energy-content.

The results obtained with the one compound so far investigated appear to show that the *spiro*-cyclic arrangement of the carbon

atoms is relatively stable. A di- and tri-cyclic arrangement appears to increase the energy content. For three- and four-rings, which are attached either to or in a six-ring, the energy-content is apparently the same as for the isolated rings.   T. S. P.

The Laws of Corresponding States. ÉMILE H. AMAGAT (*Compt. rend.*, 1913. **156**, 271—277).—A theoretical discussion of the above law, which the author considers may hold good for normal substances, deviations from the law being the result of secondary phenomena, particularly those of polymerisation. This is borne out by the fact that, of the organic compounds considered, the alcohols, which exhibit a tendency to polymerise, show the widest deviation from the law. He further replies to some criticisms of Mathias (*Congrès du froid*, 1912).   W. G.

The Elements of Energy. JACQUES DUCLAUX (*Compt. rend.*, 1913, **156**, 142—144).—A theoretical discussion of the relationship between the element of energy, as defined by Planck, being the smallest amount of energy which can intervene in a radiation of wave-length λ, expressed by $\epsilon = 19.6 \times 10^{-17}/\lambda$, and the element of energy from the Pictet-Trouton law, the smallest amount of energy which can intervene in a chemical transformation or in a change of state at a temperature T, $\epsilon_1 = 9.5 \times 10^{-16} T$. Taking the case of a dark body emitting rays entirely of wave-length λ_0 at a temperature T_0, the author finds the ratio ϵ/ϵ_1 is very close to unity.   W. G.

The Molecular Association of Liquids. I. ALEXIUS J. BATSCHINSKI (*Zeitsch. physikal. Chem.*, 1913, **82**, 86—89).—Polemical. An answer to the criticism of Tyrer (A., 1912, ii, 739) on the author's calculations of critical temperature (A., 1911, ii, 189).   J. F. S.

The Molecular Association of Liquids. II. ALEXIUS J. BATSCHINSKI (*Zeitsch. physikal. Chem.*, 1913, **82**, 90—92).—The author has calculated the metacritical temperature and association factor by means of the formula deduced by him (A., 1902, ii, 444) for propyl, *iso*propyl, butyl, *iso*butyl, amyl and allyl alcohols, and for formic, propionic, butyric, and *iso*butyric acids at a series of temperatures.

He also calculates the metacritical density of water from the atomic critical volumes of hydrogen and oxygen, and thus is able to arrive at the metacritical temperature for water. The result is the same as that previously obtained by him by the method quoted above.   J. F. S.

A Method for the Determination of the Density of Solid Substances. J. L. ANDREAE (*Zeitsch. physikal. Chem.*, 1913. **82**, 109—114. See also A., 1911, ii, 469).—A method is given for the determination of the density of solid substances which are either very soluble or lose water of crystallisation very easily. The determinations are effected in a dilatometer, which consists of a bulb *a*

of about 10 c.c. capacity, which is connected by means of a narrow tube b with a wider tube d. The volume of the bulb is known as well as that of the tube b, which is also graduated. The method consists in placing about 20 grams of the carefully dried crystals into d; should these contain water of crystallisation, the water content is first of all accurately determined. Then the whole is weighed, the salt is then washed down into the bulb a, and sufficient water is added to completely dissolve all the solid. The tube is then placed in an inclined position and heated until the liquid stands in the narrow tube. Then the whole is weighed again; thus the weights of crystals and water are known as well as the sum of the volumes at a given temperature. If then the solubility of the substance at that temperature and the density of the mother liquor is known, it is obvious that the volume of the mother liquor and consequently the volume of the crystals must be known. Hence the density, unaffected by efflorescence or absorbed air, is known. The author has compared the values obtained by this method with the values obtained by other methods for substances which are not easily changed, and comes to the conclusion that by this method the density of a solid can be obtained with the same degree of accuracy as obtains in the case of gases.   J. F. S.

Normal and Abnormal Cases of Specific Volume of Binary Liquid Mixtures. H. S. VAN KLOOSTER (*J. Amer. Chem. Soc.*, 1913, **35**, 145—150).—It has been shown by Hyde (A., 1912, ii, 1138) that when p-nitrotoluene is dissolved in carbon disulphide, the specific gravity of the solution is less than that of carbon disulphide itself, although p-nitrotoluene has a higher specific gravity than carbon disulphide. Considerations, based chiefly on Hubbard's work (A., 1910, ii, 809), are now advanced which indicate that this phenomenon cannot be regarded as abnormal, and reference is made to a really abnormal case, that of chloroform and ether, which was recorded by Guthrie (A., 1885, 339).   E. G.

A Relation between the Atomic Volumes of the Elements and their Power of Forming Complex Compounds. G. HIRSCH-FELDT HANSEN (*Zeitsch. anorg. Chem.*, 1913, **79**, 322—326).—Elements of small atomic volume have the greatest tendency to form stable complex groups. This principle is illustrated by an arrangement of the elements according to atomic volume.   C. H. D.

Viscosity and its Significance for the Chemistry of Celluloid in Theory and Practice. H. SCHWARZ (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 32—42).—An account is given of the application of viscometric methods in the investigation of nitrocellulose, and the changes which it undergoes in solution. From measurements of the viscosity of solutions of nitrocellulose in camphor-alcohol, ether-alcohol, and in acetone, it is found that the viscosity increases very rapidly with increase in concentration, and that the solutions exhibit the phenomena of ageing. The ageing is accompanied by a very considerable increase in the viscosity, which is more pro-

nounced in the case of the more concentrated solutions. The influence of the nitration process, including the washing and bleaching processes, on the viscosity of nitrocellulose solutions is also examined, and the question of the molecular weight of cellulose is discussed in reference to the viscosity data.   H. M. D.

Change of the Surface Tension of Mercury on the Addition of Metals. FRIEDRICH SCHMIDT (*Ann. Physik*, 1912, [iv], 39, 1108—1132).—The influence of small quantities of various metals on the surface tension of mercury has been examined. The surface tension data were obtained by a method involving the measurement of the dimensions of the wave forms which are set up in the jet of liquid which issues from a tube provided with an elliptically shaped aperture. For this purpose the mercury or amalgam jet was photographed, and the required dimensions obtained by measurement of the negatives by means of a micrometer microscope. In addition, the times required for the outflow of equal volumes of mercury and the amalgams were determined, and from these data the ratio of the surface tensions can be calculated.

The observations show that the metals examined can be divided into three groups. Even at the highest concentrations investigated (about 2%), zinc, cadmium, thallium, gold, tin, and lead produce very little change in the surface tension of the mercury. The alkaline earth metals and lithium increase the surface tension to a very considerable extent. Traces are sufficient to produce an appreciable increase, and when the concentration of the added metal amounts to 0·003 to 0·006%, the influence of the addition of a further quantity is relatively small. Sodium, potassium, rubidium, and cæsium reduce the surface tension very markedly. In the case of the first three alkali metals the influence is very small at the lowest concentrations; larger quantities have a relatively very much greater effect, but if the concentration of the alkali metal is still further increased the diminution of the surface tension becomes much less pronounced. The interval of concentration for which the influence of the alkali metal is greatest, varies considerably from one member of the group to another. In the case of cæsium, the initial stage appears to be absent, the smallest traces producing a lowering of the surface tension.

From the observations it is evident that, in general, metals belonging to the same periodic group have a similar action on the surface tension of mercury. When the change in the surface tension is plotted as a function of the atomic weight of the added metal, a periodic curve is obtained.

In the group containing the alkali metals and gold, and in that which contains the alkaline earth metals, lithium and thallium, the surface tension of the amalgam is found to increase with the melting point of the dissolved metal.   H. M. D.

Internal Friction of Binary Systems. Characteristics of Definite Compounds. NIKOLAI S. KURNAKOV and S. F. SHEMT- SCHUSHNI (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1964—1991).—The

authors have investigated, at various temperatures, the viscosities of the following binary systems, which form definite compounds (thiocarbamides) and at the same time remain liquid and homogeneous: allylthiocarbimide and piperidine; phenylthiocarbimide and diethylamine; [with V. ZEJLIGER] allylthiocarbimide and methylaniline; [with A. ARSENEV] ethylthiocarbimide and piperidine.

The viscosity isotherms if these systems consist of two separate branches, which are convex to the composition axis, and intersect at an angle (increasing in acuteness as the temperature is lowered) in a maximum corresponding with equimolecular proportions of the components. A similar form is exhibited by the curves connecting the temperature-coefficient of viscosity with the composition. This "rational" type of curve represents an addition to the three types given by Dunstan and Wilson (T., 1907, **91**, 83).

The intersection of the branches of the viscosity isotherms in a rational maximum is an example of the break in continuity indicated by Mendeléev on the basis of his views on the nature of solutions. Assuming that the two branches of the viscosity isotherm belong to one and the same curve, the maximum points of diagrams of the rational type may be compared with singular or nodal points of curves of the third and higher orders. These points may be termed "Dalton points," as they characterise phases containing chemical compounds, which are subject to the laws of constant and multiple proportions.

Measurements of the viscosity of liquid systems represent one of the most sensitive methods of investigating the formation of chemical compounds and of determining their purity.

The system consisting of allylthiocarbimide and the tertiary base, pyridine, which form no substituted thiocarbamide, gives a viscosity curve totally different from those described above, the value of η_{25} for a mixture of the constituents in equimolecular proportions being rather less than the arithmetic mean of the values for the pure components.   T. H. P.

Influence of Temperature on the Turbulent Flow. CL. SCHAEFER and G. FRANKENBERG (*Physikal. Zeitsch.*, 1913, **14**, 89—93. Compare Sorkau, A., 1912, ii, 900).—The conclusions drawn by Sorkau from his observations on the flow of liquids in the turbulent condition are criticised. The view that the influence of temperature on the rate of flow in the first stage of turbulence is the same for all liquids is shown to be untenable, a theoretical argument being advanced which indicates that the temperature-coefficient is dependent on the specific nature of the liquid. From the hydrodynamic equations, a formula is deduced for the temperature-coefficient which is in good agreement with the experimental data.

In a similar manner, it is also shown that the supposed lack of a temperature effect in the second and third stages of turbulence is inconsistent with the facts, and that the actual temperature variation may be expressed by formulæ derived in the same way from hydrodynamic equations.

It is further shown that the observed temperature variation of the transition from the first to the second stage of turbulence is determined by the same condition, which has been shown by Reynolds to regulate the influence of temperature on the transition from the condition of steady flow to that of primary turbulent flow.

H. M. D.

Turbulence Viscosity. GUSTAV MIE (*Physikal. Zeitsch.*, 1913, **14**, 93—95. Compare Sorkau, A., 1912, ii, 900, and preceding abstract).—The irregular grouping of the experimental points on the diagram, which is obtained by plotting the rate of flow as a function of the pressure, is considered to be due to the instability of the flow under the conditions which obtain in the second and third stages of turbulence, and not to mere accidental errors of observation. If this is the case, the real influence of pressure on the rate of flow in the turbulent condition will not be obtained by simply drawing a mean curve through the experimental points on the diagram. The probable nature of the true curve is discussed in reference to Sorkau's data for ethyl acetate, chloroform, and acetone.

H. M. D.

Determination of the Degree of Dissociation of Molten Silver Chloride and Silver Bromide. GÜNTHER SCHULTZE (*Zeitsch. Elektrochem.*, 1913, **19**, 122—126).—The author shows that when sodium glass is dipped into molten silver salts, silver ions diffuse into the glass and sodium ions diffuse into the silver. Under constant conditions the quantity of silver which diffuses is proportional to the concentration of the silver ions for small concentrations. The relation between the quantity of silver diffusing and the concentration of the silver ions is obtained by introducing small quantities of sodium salts of the same anion, and so reducing the silver ion concentration, and then determining the amount of silver which has diffused. From two such experiments, using small but different quantities of the sodium salt, it is possible to calculate the factor which gives the desired relationship by means of the law of mass action. Consequently it is easy to determine the degree of dissociation directly from the amount of diffused silver. From the experiments the values for silver chloride and silver bromide are found to be $AgCl = 1.17 \times 10^{-3}$—$1.35 \times 10^{-3}$ at $461°$, $AgBr = 2.35 \times 10^{-4}$ at $450°$. These values agree well with those of Abegg obtained from measurements of the decomposition potential (A., 1900, ii, 5).

J. F. S.

Method of Calculation of the Constant of Capillarity. The Eötvös-Ramsay Rule. The Coefficient of Compressibility of Liquids. PETRU BOGDAN (*Zeitsch. physikal. Chem.*, 1913, **82**, 93—108).—A theoretical paper in which it is shown: (1) that the molecular surface energy, calculated from the values $\gamma = \frac{1}{2} g r h \rho$, changes in a linear manner with temperature down to the critical point; (2) that in calculating the surface tension of liquids it is unnecessary to subtract the orthobaric density of the vapour from

the density of the liquid; (3) the coefficient of elasticity of a liquid is equal to the internal pressure, and that the product of the internal pressure and the coefficient of compressibility of a liquid is equal to unity; (4) that between the coefficient of elasticity, the internal pressure, and the vapour pressure of a liquid the relationship $E = P + p$ holds.   J. F. S.

The Theory of Osmotic Pressure. JOHANNES J. VAN LAAR (*Zeitsch. physikal. Chem.*, 1913, **82**, 223—224).—The author criticises the formulæ derived for osmotic pressure of solutions by Stern (this vol., ii, 28; see also A., 1895, ii, 107; 1906, ii, 526; 1908, ii, 1018; Lewis, A., 1908, ii, 465).   J. F. S.

Diffusion through Rubber Membranes. WILLIAM J. GIES, JACOB ROSENBLOOM, WILLIAM H. WELKER, GEORGE D. BEAL, and GEORGE A. GEIGER (*Biochem. Bull.*, 1912, **2**, 55—86).—On the assumption that the diffusion of a solute depends largely on the chemical affinity of the membrane and the materials on each side of it, study was directed to what occurs in membranes made of rubber in relation to substances soluble in ether. The experiments recorded deal with fats, alkaloids, lipoids, proteins, and pigments.
                                                                      W. D. H.

General Characters of the Actions between Molecules. MARCEL BRILLOUIN (*Ann. Chim. Phys.*, 1913, [viii], **28**, 48—77).—A theoretical paper and the first of a series in which the author proposes to consider the mechanical properties of matter, regarded as composed of a large number of identical particles (molecules) which may be isotropic or anisotropic, in equilibrium, in motion due to the action of a homogeneous medium having a mean uniform movement, or undergoing translatory movement in any sense. In this paper the conditions which govern the mutual mechanical action of molecules are discussed, and the views advanced by Schröder, by Sollas, and by Barlow and Pope (T., 1906, **89**, 1723) are examined. The author considers that the form of the neutral zone (in which mutual action between molecules is nil), and therefore crystalline form, may have a direct relationship to the constitution of the molecule, in so far as this depends on valency, but the molecular volume is, in addition to that, dependent on the nature of the atoms.   T. A. H.

The Partial Miscibility of Liquids. ÉMILE BAUD (*Compt. rend.*, 1913, **156**, 317—320. Compare A., 1912, ii, 233, 331).—Studying a mixture of acetic acid and *cyclo*hexane the author has determined the temperature of crystallisation of the acid in the solvent at various concentrations, and has plotted a temperature-concentration curve. For conditions of partial miscibility the temperature at which crystallisation commences must be a minimum point on the above curve.   W. G.

The Atomistic Theory of Polymorphism. GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1913, **82**, 172—200).—A theoretical paper in

which the following points are discussed: (1) Polymorphism and the molecular composition of the liquids. The conclusion is drawn in this connexion that in liquids which have a value for $-d(\alpha v i)/dT$ less than 2·00, that is, liquids which are associated, more than one thermodynamic crystal group may separate, whilst for liquids which have a value more than 2·00 only one crystal group can separate. (2) The crystallisation of different crystal groups from associated liquids. (3) The characteristics of association in crystals. (4) The thermal characteristics of the forms of a thermodynamical crystal group.   J. F. S.

Jellies. RICHARD ZSIGMONDY and WILHELM BACHMANN (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 16—18. Compare A., 1912, ii, 1149). —Polemical against von Weimarn (this vol., ii, 32). It is pointed out that the observations relating to the morphological structure of gelatinised soap solutions has not been put forward as evidence in support of the crystalline nature of jellies in general. It would appear that von Weimarn and the authors do not agree in respect of the question as to what properties determine whether or not a substance belongs to the group of jellies.   H. M. D.

Reversible Coagulation Processes. SVEN ODÉN and E. OHLON (*Zeitsch. physikal. Chem.*, 1913, **82**, 78—85).—Colloidal solutions of silver and sulphur in 1% solutions were placed in a centrifugal machine and treated with a series of different concentrated solutions of electrolytes. In the case of the silver solution, ammonium nitrate was used, whilst with the sulphur solutions, sodium chloride was employed. The addition of the electrolyte caused coagulation, which was completed rapidly by centrifugalising. Then by more rapid centrifugalising the coagulating electrolyte was removed, and the solution made up to its original volume with the pure solvent, when the colloidal substance again passed into solution. The solution was then examined by ultra-microscopic methods, and the number and size of the particles determined. From these experiments the authors state that there is no change in the size of the particles, even after many coagulations and re-solutions, and that the individual particles maintain their identity in the coagulated mass.   J. F. S.

Method for the Determination of the Size of Colloidal Particles. A. DUMANSKI, E. ZABOTINSKI, and M. EVSÉEV (*Zeitsch. Chem. Ind. Kolloids*, 1913, **12**, 6—11).—On the assumption that the colloidal particles are spherical in form, it is shown that the radius of the spheres may be obtained from the formula:

$$r = \sqrt[3]{3v(\delta + c - d_s)/4\pi n \delta},$$

in which n is the number of particles in volume v, c the concentration of the colloidal solution, δ the density of the solvent, and d_s that of the solution.

From the data for three colloidal solutions it is found that the value of r given by this equation is from one and a-half to three

times as large as the value obtained from Stokes's equation for the rate of segregation of the particles.

Other formulæ for the radius of the colloidal particles are deduced by combining Einstein's equation, $\eta/\eta_0 = 1/(1-\phi)$, for the relation between the viscosities of the solution (η) and the solvent (η_0) and the volume (ϕ) occupied by the colloidal substance with Stokes's equation. These are applied in the calculation of the dimensions of the particles in colloidal solutions of arsenious sulphide which have been investigated at $0°$, $20°$, and $50°$.

<div style="text-align:right">H. M. D.</div>

The Application of the Principles of Colloidal Chemistry to the Considerations of the Question of Specificity. Wolfgang Ostwald (*Biochem. Zeitsch.*, 1913, **48**, 225—229).— Michaelis and Davidsohn (this vol., i, 121) have recently shown that the formation of specific agglutins and precipitins is largely independent of the hydrogen ion concentration, and is to a large extent independent of the electrical charge of the particles concerned in the precipitate formation. They draw the conclusion from these results that the cause of precipitation is essentially of a chemical character, and that the general principles of colloidal chemistry are not applicable to these phenomena. To the latter statement the author takes exception, on the ground chiefly that electrical factors are not the only ones to be taken into account as the cause of precipitation from colloidal solutions. He quotes instances to show that adsorptive precipitation can be produced by two substances, both of which have the same kind of electrical charge (toxins and antitoxins), and, furthermore, certain concentrated electolytes which can neutralise and discharge a colloid (gold sols) do not always produce precipitation. Other important factors which determine the precipitability of a colloid, such as the surface tension at the interfaces, are not influenced solely by the electrical charges, but other chemical and physical characters must be taken into account, such as the grade of the dispersion, and the degree of hydration of the colloid.

<div style="text-align:right">S. B. S.</div>

Reciprocal Salt Pairs and Double Ternary Salt Mixtures. Ernst Jänecke (*Zeitsch. physikal. Chem.*, 1913, **82**, 1—34. See also A., 1908, ii, 808; 1909, ii, 872; 1912, ii, 750).—A theoretical mathematical paper. The relationship between weight % and molecules % curves for reciprocal salt pairs is discussed, and a new method of representing the weight relationships introduced. The solid-liquid relationships of reciprocal salt pairs is discussed, making use of the Z-function of the thermodynamic potential. The Z-function is defined by the equation $Z = E - TS + Pv$, where E is the internal energy, S the entropy, and T, P, and v the absolute temperature, pressure, and volume. The reciprocal pairs are discussed for cases where one, two, three, four, five, and more solid phases are present. Instances are cited of pairs which will probably show the properties theoretically deduced. The equilibrium of double ternary mixtures $(M'M''M''')(S'S'')$ or $(M'M'')(S'S''S''')$, where $M'M''M'''$ represent

metals, $S'S''S'''$ acid radicles, are discussed for the cases where one, two, three, four, five, six, and more than six solid phases are present.
J. F. S.

The **Partial Pressures of Ternary Mixtures.** FRANS A. H. SCHREINEMAKERS (*Zeitsch. physikal. Chem.*, 1913, **82**, 56—58).—A mathematical paper, in which from Duhem-Margules equation for binary solutions (A., 1901, ii, 227) the author deduces an expression for ternary mixtures which has the form:

$$x_1 dl\pi_1 + y_1 dl\pi_2 + (1 - x_1 - y_1) dl\pi_3 = 0,$$

in which π_1, π_2, and π_3 are the partial pressures of the constituents in the gaseous phase, and x_1, y_1 and $(1 - x_1 - y_1)$ the quantities of the substances in the liquid. This equation is shown to be a special case of the Duhem-Margules equation.   J. F. S.

The **Quadruple Point and Triple Curves in Binary Systems** FRANS A. H. SCHREINEMAKERS (*Zeitsch. physikal. Chem.*, 1913, **82**, 59—70).—The author considers the relationships, on the basis of the phase rule, of binary systems which can exist in four phases. The changes which occur when pressure, temperature, or concentration is effected at the quadruple point are discussed. The conclusions arrived at are applied to the systems H_2S—H_2O (Scheffer, A., 1911, ii, 264, 870) and iodine-chlorine (Stortenbeker, A., 1889, 102).   J. F. S.

The **Equilibria in the System Barium Chloride, Sodium Nitrate, Barium Nitrate, Sodium Chloride, and Water.** ANGELO COPPADORO (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 842—850. Compare A., 1912, ii, 441).—Of the four ternary systems comprised in this quaternary system, that of sodium chloride, barium chloride, and water has been investigated at 30° by Schreinemakers and de Baat (*Zeitsch. physikal. Chem.* 1909, **65**, 587). The other three systems and the quaternary system have now been investigated at the same temperature, and the present paper gives the results of this work in a number of tables.   R. V. S.

Equilibria between Potassium Hydrogen Carbonate and **Salts of Magnesium, Nickel, and Cobalt.** T. NANTY (*Ann. Chim. Phys.*, 1912, [viii], **27**, 5—89 ; 1913, [viii], **28**, 77—208).—The results already recorded (A., 1911, ii, 103, 282) for the action of potassium hydrogen carbonate on salts of magnesium are described in greater detail, and a mathematical discussion of the whole subject is given. It is then shown that the action of potassium hydrogen carbonate on nickel salts is strictly analogous to its action on magnesium salts, both actions being reversible in the ordinary sense. These results are therefore at variance with those observed by Engel (A., 1886, 121). Cobalt salts behave differently, no equilibrium being reached in this case.

The conditions prescribed by various authors, and especially Engel (*loc. cit.*) for the preparation of magnesium carbonate, $MgCO_3,3H_2O$, and potassium hydrogen magnesium carbonate,

$KHCO_3, MgCO_3, 4H_2O$, are examined, and shown to be inaccurate and incomplete, and experimental data supporting this conclusion are quoted. The conditions under which either or both salts may be formed are then determined by the use of Gibbs' graphic method for ternary mixtures, and it is shown that these conditions can be verified experimentally; thus at temperatures 7--8°, 15°, and 26--27° the composition of the precipitate is independent of the concentration of the magnesium salt, and depends only on the concentration of the potassium hydrogen carbonate in the generating liquid. At 7--8°, 2·2% of the latter salt is the critical value, anything below that giving magnesium carbonate, and anything above it the double carbonate. At 15° the critical value is about 4%, and at 26--27° about 6%. The only secondary reaction is the reversible decomposition of the double carbonate by water, and to this is due the variation of the critical value with temperature.

The second paper begins with a mathematical and experimental investigation of the conditions necessary for the formation of either carbonate, and methods of calculating the composition of solutions which on admixture will give a precipitate of the required composition are given, with experimental verifications.

The equilibrium conditions for the formation of the double carbonate and its decomposition by water are then investigated, and shown to be identical for the same temperature, under atmospheric pressure. The velocity of the reaction in either direction at the same temperature and pressure is proportional to the difference between the initial and final concentration of potassium hydrogen carbonate in the solution; the velocity constant increases with the temperature.

A similar but less detailed study has been made of the formation of nickel carbonate, $NiCO_3, 3H_2O$, and of the double carbonate, $NiCO_3, KHCO_3, 4H_2O$, and the results are completely analogous to those obtained for the corresponding magnesium salts.

Cobalt salts on precipitation with potassium hydrogen carbonate give a basic carbonate, $CoCO_3, CoO, 5H_2O$, and a double carbonate, $CoCO_3, KHCO_3, 4H_2O$, the former amorphous, the latter crystalline. No combination takes place between cobalt carbonate and potassium hydrogen carbonate, and no equilibrium is reached in the action of water on the double carbonate, referred to above.

T. A. H.

Displacement of the **Primary Amylamines** by Gaseous Ammonia. Félix Bidet (*Compt. rend.*, 1913, **156**, 315--317).-- A study of the equilibrium pressures of amylamine hydrochloride and its *iso*-isomeride in the presence of gaseous ammonia at different temperatures. The values for the straight-chain compound are considerably lower than those for the *iso*-compound at low temperatures, but the values become practically equal at 50°. The figures indicate the existence of several definite basic hydrochlorides, the state of equilibrium being a function of the concentration of the ammonia.

W. G.

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Influence of Temperature on the Velocity of Chemical Reactions. II. B. SCHVECOV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, Phys. Part, 516—519).—In a previous paper (this vol., ii, 124), the author has suggested the characterisation of the influence of temperature on the velocity of chemical reactions by the logarithmic temperature-coefficient, η, expressed by $(K_2/K_1)^{\frac{\log \rho}{\log T_2 - \log T_1}}$, where K_1 and K_2 are the respective velocity constants determined for the absolute temperature T_1 and T_2, and ρ is a constant. From this expression it follows that constancy of η requires the fulfilment of the condition $d\log K / d\log T = \text{constant}$.

Starting from the assumption that chemical reaction is a consequence of the reacting molecules impinging one on the other with a sufficient degree of violence, the author now shows mathematically that, in the case when molecules of only two kinds react, $d\log K / d\log T$ has the constant value 1·5. The assumptions made in arriving at this result are that the reaction shall be non-reversible, and that it shall take place either in a gaseous medium or in dilute solution. For reversible reactions, constancy of the logarithmic temperature-coefficient is to be expected only when the velocity of the reverse reaction is virtually independent of the temperature.   T. H. P.

The Action of Carbonic Acid on Alkalis and Alkaline Earths as a Time Reaction. DANIEL VORLÄNDER and WALTER STRUBE (*Ber.*, 1913, **46**, 172—181).—When a solution of calcium hydroxide, coloured red with phenolphthalein, is rapidly mixed with an aqueous solution of carbon dioxide of slightly more than the equivalent strength, there is no immediate disappearance of the red colour. The time necessary for decolorisation may vary from a few minutes to several days, increasing with the dilution of the solutions. As the excess of carbon dioxide is increased, the time diminishes, but still remains of the order of several seconds when about four times the equivalent of carbonic acid is used. If a precipitate forms, it is deposited before decolorisation occurs. These results were shown not to be due to alkali being dissolved from the glass, or to other such side-reactions.

Similar results were obtained with solutions of barium and sodium hydroxides, but the times necessary for the disappearance of the red colour were very much less, being generally of the order of a few seconds, unless, in the case of barium hydroxide, the dilutions are very great. Lowering the temperature increases the time.

The authors consider that it is probable that the above phenomena are due to the hydration of carbon dioxide to carbonic acid not being complete in aqueous solution, and taking place only slowly during the neutralisation. No other weak acids, such as hydrogen sulphide, acetic acid, etc., gave similar results.

It is found that pure and well-washed calcium carbonate gives an alkaline reaction to water.

The results show that calcium hydroxide cannot be used for the estimation of the free carbonic acid in water.   T. S. P.

The Slow Neutralisation of Carbonic Acid. ALFRED THIEL (*Ber.*, 1913, **46**, 241—244).—Polemical against Vorländer and Strube (preceding abstract). The author points out that according to experiments which are to be published later, the hydroxides of the alkaline earths are not suitable for studying the actual time-reaction with carbonic acid, owing to the gradual alteration in condition (" ageing ") which takes place of the carbonates formed. The author has previously observed the time reaction between carbonic acid and sodium hydroxide (*Sitzber. Ges. Wiss. Marburg,* Nov., 1912), and given the same interpretation as Vorländer and Strube (compare also MacBain, T., 1912, **101**, 814).   T. S. P.

Kinetic Investigation of the Action of Carbon Monoxide on Solutions of Potassium Permanganate. GERHARD JUST and YRJÖ KAUKO (*Zeitsch. physikal. Chem.*, 1913, **82**, 71—77).—The experiments described were carried out in exactly the same way as the previous experiments on the action of hydrogen on potassium permanganate (A., 1911, ii, 494). It is shown that in neutral solutions of potassium permanganate the rate of reaction is proportional to the concentration of the carbon monoxide. It was found necessary, in order to get effective mixing of the gas and solution, to rotate the reaction vessels 5000 times per minute. The concentration variations were brought about by mixing the carbon monoxide with nitrogen. The reaction is shown to take place, in the first place, between one molecule of carbon monoxide and one molecule of potassium permanganate with the probable formation of an unstable quinquevalent manganese derivative. The influence of temperature was investigated, and found to be such that an increase of $10°$ doubled the velocity of reaction. The reactions were also carried out with a series of hydrogen carbon monoxide mixtures, from which it is evident that both substances react normally without any influence on one another.   J. F. S.

The Velocity of the Reaction of Bromine and Aqueous Solutions of Monohydroxy-Aliphatic Alcohols. ELISABETH RÓNA (*Zeitsch. physikal. Chem.*, 1913, **82**, 225—248).—The velocity constants for the reactions between bromine and methyl, propyl, *iso*propyl, butyl, *iso*butyl, and *tert.*-butyl alcohols are determined by the method adopted by Bugarsky (A., 1910, ii, 281) for ethyl alcohol. The reactions were carried out at $25°$, and with the exception of those with methyl and *tert.*-butyl alcohols all occurred in two stages, the alcohol being first oxidised to aldehyde or ketone, and this then to acid. The velocity constants were determined for both reactions, as well as the total reaction constant. The constants increased with the molecular weights of the normal alcohol, the value of the first constant increasing less than the constant for the second reaction, the amount of increase slowly increasing as the molecular weight increases. The *iso*-alcohol has in both cases larger velocity constants than the corresponding normal alcohol, and the amount of increase between two consecutive *iso*-alcohols is much greater than that between the corresponding normal alcohols.

J. F. S.

Gradual Hydrolysis. CARL L. WAGNER (*Monatsh.*, 1913, 34, 95—170).—The hydrolysis of salts of weak bases with strong acids and of strong bases with weak acids can be conveniently studied by the increase in conductivity which is observed when the requisite dilution is reached. In some instances the increase is not sudden, but proceeds at a measurable speed, and three explanations have been offered to account for this phenomenon. In the case of stannic chloride, which is practically a non-conductor, Kovalevski (A., 1900, ii, 256) suggested that the scarcity of ions accounted for the sluggishness of the process. The hydrolysis of ferric chloride has been assumed to proceed through the stages:

$$FeCl_3 \longrightarrow FeCl_2 \cdot OH \cdots FeCl(OH)_2 \cdots Fe(OH)_3$$
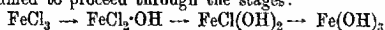
(compare Antony and Giglio, A., 1896, ii, 250; Goodwin, A., 1897, ii, 16; and Malfitano, A., 1912, ii, 337). A 'third explanation involves hydrate isomerism as exhibited by green and violet chromium chloride. It has therefore been necessary to conclude that just this particular ionic reaction is measurably slow, or to assume purely theoretical ions, or to construct co-ordinate compounds for each case.

It is remarkable, however, that in all the observed cases, either the weak base or the weak acid shows a great tendency to form a colloidal solution, and the author therefore offers a simple explanation of the gradual increase in conductivity which is based on a conception of the changes in superficial magnitude of the colloid. As the result of hydrolysis, the metallic hydroxide (or the acid) is liberated as a highly-dispersed phase, on the enormous surface of which the liberated acid (or base) is at first completely adsorbed. In the process of time the particles become larger, that is, the surface of the dispersed phase rapidly diminishes, and therefore the adsorbed acid or base is able to enter the continuous phase, the solution.

The theory is supported by experiments on the conductivity of ferric alum in various concentrations where, contrary to the experience of Goodwin with ferric chloride (*loc. cit.*), the solutions get turbid, deposit a precipitate, finally become colourless, and the conductivity does not reach a constant, neither does it attain to the value for solutions of sulphuric acid and potassium sulphate containing the equivalent of $\cdot SO_4$ ions. The addition of protective colloids, such as carefully washed agar-agar, or, better still, gelatin, retards the growth of the conductivity. It also prevents the precipitate from settling in a dense form, so that the acid is washed out by the solution to a greater extent, and hydrolysis apparently proceeds farther. When the precipitate begins to form, however, the protective colloid is carried with it, and is thus removed from further action.

Goodwin found that ferric chloride solutions remained perfectly clear, developed the brown colour of ferric hydroxide sols, and attained a conductivity which agreed with the equivalent quantity of hydrochloric acid. This experience is confirmed, and the explanation offered that the requisite diminution in the surface of the dispersed phase takes place within the region of colloidal

solution, that is, without the formation of macroscopic particles, and therefore equilibrium is more quickly reached. The addition of gelatin again retards the growth of the conductivity to a great extent, even when allowance is made for the smaller conductivity of hydrochloric acid in a gelatin solution. The different behaviour of ferric alum is due to the intensive coagulating action of the bivalent ·SO₄ ions, and the effect of these on a ferric chloride solution is extremely pronounced. The addition of $1/160,000$ of an equivalent of potassium sulphate produces a noticeable difference in the conductivity curve (a possible test for traces of ·SO₄ ions) and more than $1/2000$ of an equivalent causes turbidity and precipitation. The final values are not as high as those for the pure solution plus the sulphate, since the coagulating ions are adsorbed on the ferric hydroxide. This is shown by the fact that the addition of ·SO₄ ions to an already completely hydrolysed ferric chloride solution causes coagulation and a fall in the total conductivity.

The influence of foreign electrolytes also explains some discrepancies which were observed with ferric acetate and aluminium acetate. When these solutions were prepared by double decomposition, or by casual solution of the hydroxide, the conductivities remained constant for a great length of time. A ferric acetate solution made from freshly precipitated hydroxide which had been completely extracted by conductivity water, however, showed the same gradual hydrolysis and rise in conductivity towards the value for acetic acid, and the effect of potassium sulphate was the same as before.

J. C. W.

Saponification in Stages. III. Hydrolysis of Acid Amides and Nitriles. Nicolas von Peskov and Julius Meyer (*Zeitsch. physikal. Chem.*, 1913, **82**, 129—171. Compare A., 1907, i, 462, 819 ; 1909, ii, 391, 803).—In the first part of the paper a general formula is deduced for the velocity constant of a reaction which takes place between two substances in four stages; thus the reaction $RP^1P^2 + MN$ is considered to occur in the stages $RP^1P^2 + MN = RP^1M + NP^2$, $RP^1P^2 + MN = RP^2M + NP^1$, $RP^1M + MN = RM_2 + NP^1$, and

$$RP^2M + MN = RM_2 + NP^2 ;$$

all four reactions are assumed to have different reaction velocities. The general formula is then simplified to make it adaptable to special cases. The simplified forms are the same as those deduced by Meyer, from other considerations, for the hydrolysis of the normal esters of dibasic acids. In the experimental part of the paper, the hydrolysis of amides and nitriles of monobasic acids and of amides of dibasic acids, are considered. The experiments were carried out with acetamide, formamide, propionamide, butyramide, isobutyramide, valeramide, and hexonamide; acetonitrile and propionitrile; malonamide and succinamide. The amides or nitriles were mixed in weighed quantities with known amounts of hydrochloric acid or sodium hydroxide in flasks which were kept at 18° or 25° in a thermostat. At measured intervals of time 10 c.c. of the reaction mixture were withdrawn, and treated with an excess

of sodium hypobromite, and the quantity of nitrogen formed measured. It is shown that the amides of monobasic acids are hydrolysed more rapidly by alkalis than by acid, although here the difference is not so marked as in the case of esters of dibasic acids; in the latter case Meyer (*loc. cit.*) showed that the ratio between the two velocities was about 3500, whilst in the present case it is only about 6. The reaction in every case is strictly bimolecular, and has a temperature-coefficient of about 2·6 for 10° change of temperature. In the experiments with nitriles, it was found that the reactions occurred too slowly with acids, and consequently experiments were only made with alkalis. In this case it was found that equally good reaction constants could be obtained by using the equations for either the two-step reaction (that is, nitrile $\rightarrow$ amide $\rightarrow$ acid) or the one-step reaction (that is, nitrile $\rightarrow$ acid). From this the authors draw the conclusion that the velocity of the first reaction is extremely great when compared with that of the second stage, and consequently the second stage is the only one which conditions the measurement. The temperature-coefficient of these reactions lies in the region of 2·6, as in the case of the amides. An anomalous case is presented by the hydrolysis of the amides of dibasic acids, inasmuch as no reaction constant which is constant can be obtained. The values of k decrease very rapidly, and after some time reach a figure which displays approximate constancy. This is explained by the authors as due to the fact that the first half of the reaction is abnormal, whilst the second half is normal. It is also shown that both amido-groups are not hydrolysed at the same rate. With acids the constant k_1 is smaller than k_2, whilst with alkalis k_2 is smaller than k_1. This is explained by the fact that there will be a repulsion between the negatively charged acid amide radicle, $NH_2 \cdot CO \cdot R \cdot CO \cdot O'$, and the negatively charged OH' group, whilst between the positively charged $H^{\cdot}$ ion and the acid ion there will be an attraction.　　　　　　　　　　　　J. F. S.

The Dynamics of the Change Acetochloroanilide $\rightarrow$ *p*-Chloro-acetanilide in the Presence of Acids. ALBERT C. D. RIVETT (*Zeitsch. physikal. Chem.*, 1913, **82**, 201—216).—The velocity of the change of acetochloroanilide into *p*-chloroacetanilide,

$$(C_6H_5 \cdot NAcCl \rightarrow C_6H_4Cl \cdot NHAc)$$
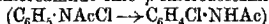
in aqueous solution by hydrochloric acid of various concentrations is investigated. It is found to be a unimolecular reaction, and the velocity increases with the concentration of the acid. The catalytic action is held to be due to the non-ionised acid alone. The relationship between the concentration of the acid and the velocity constant is expressed by the equation $k = (1-a)C(A + BaC)$, in which k is the velocity constant, C is the concentration of the acid, a the degree of ionisation of the acid, and A and B two constants which have values 0·05 and 0·22 respectively. The temperature-coefficient of the reaction is found to be 3·27 for 10° over the range 0—30°. This value agrees with the expression of Harcourt and Esson (A., 1912, ii, 923), that the ratio k/T^m is a constant; using the value $m = 34$, the value $k/T^{34} \times 10^{88} = 92$ (approx.). The reaction was also

carried out with solutions of acetic, oxalic, trichloroacetic, and sulphuric acids,• at 60°, since the reaction was too slow at lower temperatures. Constant values for k could not be obtained in any of these cases, the reactions evidently. proceeding in an abnormal manner. It is noticed that a purple coloration of the solution occurs after the reaction has been in progress for some time; 100 to 200 minutes for sulphuric and trichloroacetic acids, 300 minutes with oxalic acid, and 3000 to 4000 minutes with acetic acid. At the end of the reaction a strong reducing agent is present in the solution.

J. F. S.

Velocity of Formation of Precipitates. KASIMIR JABLCZYNSKI (*Zeitsch. physikal. Chem.*, 1913, 82, 115—121).—The author has studied the rate at which precipitates are formed from dilute solutions. The method consists in mixing measured volumes of solutions of ammonium chloride and silver nitrate of known concentrations, and observing the time required for the formation of a precipitate. The reactions are carried out in test-tubes, which are covered with a paper mantle which has a square hole cut in it. This hole is partly covered with a narrow strip of black paper. The moment at which a precipitate is judged to have been formed is that moment at which the black strip becomes invisible. The reactions were all effected in absence of actinic light. Using a normal solution of silver nitrate and adding to it an equal volume of ammonium chloride of various concentration, it is shown that the velocity diminishes . as the concentration of the ammonium chloride increases from $0·01N$ to $0·016N$, at which point it reaches a minimum. Afterwards it increases to an instantaneous precipitation as the concentration increases to normal. Similarly, starting with 5 c.c. of $0·01$ ammonium chloride, and adding an equal volume of silver nitrate solution, it is shown that the velocity decreases as the concentration of the silver nitrate increases from $0·01N$ to $0·02N$, after which it increases to an exceedingly high value as the concentration of the silver nitrate is increased to $0·5N$. The addition of increasing small quantities of ammonia causes an increase in the velocity as the concentration of the ammonia increases up to $0·006N$, whilst on the other hand the addition of sodium thiosulphate causes a retardation of precipitation as the concentration of the sodium thiosulphate increases from $0·000012N$ to $0·000120N$. The addition of alcohol decreases the velocity of precipitation. The velocity of precipitation increases 100% for an increase of $10°$ in temperature. The velocity of precipitation of silver bromide is only about one-half that of silver chloride, which the author is of the opinion points to the fact that the velocity of precipitation is not conditioned by supersaturation.   J. F. S.

Theory of the Efflorescence of Saline Hydrates. Influence of Temperature. CH. BOULANGER and GEORGES URBAIN (*Compt. rend.*, 1913, 156, 135—137. Compare this vol., ii, 34).—A mathematical discussion of the rate of efflorescence of identical crystals at different temperatures. Coupling this with laws previously deduced (*loc.*

cit.) for the rate of efflorescence of crystals of different sizes and at different stages of efflorescence, the authors have obtained an expression by which it is possible to deduce the heat of hydration from the law governing the efflorescence at two different temperatures.

. W. G.

Velocity of Reaction and Catalysis. KURT H. MEYER (*Zeitsch. Elektrochem.*, 1913, **19**, 76). —Polemical. An answer to Trautz (*ibid.*, 1912, **18**, 917) concerning the author's paper (A., 1911, i, 350).

J. F. S.

Outline of a Theory of Homogeneous Catalysis. MARTIN A. ROSANOFF (*J. Amer. Chem. Soc.*, 1913, **35**, 173—177).—Homogeneous catalysis is either direct or indirect. A direct catalyst is a substance which influences the reaction by the formation of intermediate molecular complexes, whilst an indirect catalyst is one which does not take any part in the reaction, but influences its velocity by affecting the particular conditions (such as the association or dissociation of the reacting substances) on which the reaction depends. A direct catalyst obeys the law of mass action, but an indirect catalyst does not. An equation of catalysis has been deduced which is based on the assumption that the relative change of the velocity coefficient of a reaction is proportional to the change in the concentration of the indirect catalyst. It is shown that the number of indirect catalysts possible for any given reaction is indefinitely large, and that all negative catalysts belong to this class. According to this theory, the velocity of chemical reactions is governed both by the law of mass action and a catalysis law. The equation expressing the effect of indirect catalysts has been found of great assistance in enabling the type of catalysis in any given reaction to be characterised and in thereby elucidating the mechanism of the reaction. Experimental evidence of this will be given in subsequent communications.   E. G.

Surface Combustion. WILLIAM A. BONE (*Ber.*, 1913, **46**. 5—28). —An illustrated lecture on the catalytic influence exerted on gaseous combustion by hot surfaces, delivered before the German Chemical Society.   D. F. T.

Catalytic Studies. II. Barium Ion Catalysis. EMIL ABEL (*Monatsh.*, 1913, **34**, 171—191. Compare A., 1912, ii, 927).—The addition of barium salts causes an acceleration in the oxidation of sodium thiosulphate by hydrogen peroxide. This catalytic action is not due to the mere influence of a neutral salt, for alkali salts cause no acceleration, neither is it due to the liberation of hydrogen ions according to the equilibrium, $Ba^{\cdot\cdot} + H_2O_2 \rightleftarrows BaO_2 + 2H^{\cdot}$, for free acids have no effect, and barium peroxide can hardly be expected to behave more powerfully than hydrogen peroxide. The author therefore suggests the possibility of changes in the valency of the barium ion, and since the catalytic action is also observed in the oxidation of potassium iodide with hydrogen peroxide and is therefore due to the action of the peroxide on the barium ion,

the conclusion is drawn that quadrivalent barium ions are formed. Similar results have been obtained in preliminary experiments with calcium and strontium ions.   J. C. W.

Catalysis. XIII. Reaction of Ethyl Iodide with Sodium 3-Thio-1-phenylurazole. SIDNEY NIRDLINGER, F. M. ROGERS, and SOLOMON F. ACREE (*Amer. Chem. J.*, 1913, **49**, 116—127. Compare Acree, A., 1912, ii, 1047).—In continuation of the quantitative study of the mechanism of the reactions of alkyl haloids with urazoles by determining the conductivity of urazole salts and the velocity of their reactions with alkyl haloids (Brunel and Acree, A., 1910, i, 520), an investigation has now been made of the sodium salt of 3-thio-1-phenylurazole.

The velocity of the reaction of ethyl iodide and sodium 3-thio-1-phenylurazole has been determined in solutions of concentrations from $0.3N$ to $0.025N$. The percentage ionisation of the sodium salt has been measured at the same concentrations by means of the conductivity method. By substituting the values obtained in the equation $K_n = K_i \alpha + K_m (1 - \alpha)$, satisfactory constants have been found for K_i and K_m. The results indicate that the velocity of the reaction is a function of the concentrations of both the urazole and the non-ionised urazole salt.   E. G.

The Periodic System and Atomic Weight. ALOIS BILECKI (*Zeitsch. physikal. Chem.*, 1913, **82**, 249—252).—The author divides the elements into four groups, which end respectively with helium, argon, xenon, and an unknown element. The lengths of these groups are in the ratio of the squares of the uneven numbers. It is shown that if a series of chosen numbers from 21 to 125 are multiplied by the factor 1·86, the atomic weights of some 36 of the elements are obtained with fair approximation. There is also a series of elements the atomic weights of which are whole numbers, and the author states that still a third series must exist the atomic weights of which will be found to be obtained by a combination of multiples of the numbers 1 and 1·86.   J. F. S.

The Life and Work of Marcellin Berthelot. ÉMILE JUNG-FLEISCH (*Bull. Soc. chim.*, 1913, [iv], **13**, i—cclx).—An obituary notice.   T. A. H.

Substitution of Ground Glass Stopper in Combination Barometer and Manometer. ROSS ALLEN BAKER (*J. Amer. Chem. Soc.*, 1913, **35**, 199).—Radulescu (A., 1912, ii, 37) has described a manometer in which a ground-glass stopper is substituted for the usual scaled end. The author points out that he has used a similar device on a combination barometer and manometer. The use of a mercury seal round the ground-glass stopper prevents the risk of leakage. The larger tube, of capacity 10—15 c.c., which forms the mercury cup, may be fused on to the main tube, and is easily stoppered to prevent volatilisation of the mercury.   E. G.

New Cover Glass Support. Ross ALLEN BAKER (*J. Amer. Chem. Soc.*. 1913, **35**, 200).—A convenient cover glass support can be made by fusing three pieces of glass rod together at one end, and afterwards bending them apart at equal angles and downwards to any degree desired.   E. G.

A Simple Form of Gas Generator. FRANK SHEDDEN (*J. Soc. Chem. Ind.*, 1913, **32**, 3).—A cylindrical jar, 48—50 cm. high and 18 cm. diameter, and fitted with a stopcock at the bottom, contains an inner tube, 10 cm. in diameter and narrowed at the top to a neck about 6 cm. in diameter, which is closed by a rubber stopper and glass stopcock. About 8—10 cm. from the bottom the inner tube is constricted to a diameter of 1—2 cm. The inner tube rests on a glass triangle, arranged so as to allow free circulation, and is held in place by a wooden cover, which may, if necessary, be weighted with a leaden collar.

When using powdery substances or fine-grained material, a filter plate is placed on the constriction before charging. A generator of the above dimensions will hold 5 litres of liquid and several kilos. of solid.   T. S. P.

A New Reflux and Distillation Condenser. FRANZ MICHEL (*Zeitsch. angew. Chem.*, 1913, **26**, 88).—The lower end of the condenser, which is not in the water jacket, is surrounded by a wider tube, into the side of which is sealed a tube connecting it with, and opening into, that part of the condenser tube which is in the lower part of the water jacket. The vapour from the flask, when the condenser is used as a reflux, passes into the annular space between the two tubes, and hence through the side-tube into the condenser, from which it flows back as liquid, through the central tube, into the flask.   T. S. P.

Two Lecture Experiments on the Diamond. WILHELM PRANDTL (*Ber.*, 1913, **46**, 216—217).—Moissan's method of making diamonds may be modified as follows: In a cylindrical can of sheet metal, 10 cm. in diameter by 12 cm. high, is placed another cylinder, open at both ends, of less diameter, and the space between the two filled with dry, powdered fluorspar. The inner cylinder is then filled with a mixture of 200 grams of iron thermit and 10—15 grams of powdered coke, after which it is withdrawn, so that the thermit mixture is surrounded at the sides by the fluorspar, but is in direct contact with the bottom of the sheet metal can. The can is fixed on an iron ring placed above a vessel containing mercury covered with a layer of 15—20 cm. of water, and the thermit mixture fired. The liquid iron dissolves the carbon, melts through the bottom of the can, and is quenched in the water and mercury. The iron is then treated in the usual way to obtain the microscopic crystals of diamond, which are accompanied by some doubly refracting, hexagonal plates, probably of carborundum.

The combustion of a diamond in oxygen can be conveniently shown by heating it in a quartz test-tube, fitted with a cork through

which pass inlet and exit tubes for the oxygen and products of combustion respectively. The combustion of the diamond is started by heating that part of the quartz tube on which the diamond rests with a blowpipe flame. 　　T.S.P.

Reaction between Calcium Permanganate and Ethyl Alcohol. F. ALEX. McDERMOTT (*J. Amer. Chem. Soc.*, 1913, 35, 219).—The following is recommended as a lecture experiment for demonstrating the oxidation of alcohol to aldehyde. A few fragments of calcium permanganate are dropped on a porous plate moistened with ethyl alcohol. The permanganate first scintillates and then glows for a few minutes, and irritating fumes, suggestive of formaldehyde, acetaldehyde, and acraldehyde, are produced, which, if drawn through a warm ammoniacal solution of silver nitrate, effect a marked reduction.

*iso*Amyl alcohol reacts similarly, but somewhat more slowly, but methyl alcohol and acetone do not behave in this way. 　　E. G.

Lecture Experiments Showing the Formation of Binary Liquid Eutectics. NIKOLAI S. KURNAKOV and N. N. EFREMOV (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1992—2000).—Camphene and methylthiocarbimide readily form a liquid eutectic when mixed at the ordinary temperature, the change taking place in a few seconds. Also, owing to the appreciable vapour pressures of the two components, if these are placed in separate vessels in a closed space, the liquid eutectic makes its appearance in the vessel containing the camphene after the lapse of about twenty-four hours.

The authors have investigated this system, the specimen of camphene used having b. p. 158—158·5°, m. p. 49·3°, and $[\alpha]_D + 57·4°$. The eutectic mixture is found to contain 73 mol. % of camphene, and to solidify at $-8°$. The limits of existence of the liquid phase at 15° are represented by 14% and 76·5% of methylthiocarbimide. The system forms no solid solutions of marked concentration, the two components separating in the pure state.

Other systems forming liquid eutectics at the ordinary temperature are: camphene–naphthalene; camphene–benzene; camphene–phenanthrene, and methylthiocarbimide–naphthalene, but in these cases this occurs only within much narrower concentration limits than with camphene–methylthiocarbimide. The following compositions (mol. %) and solidifying points of the liquid eutectic were determined: (1) 86 camphene + 14 naphthalene, $+7·5°$; (2) 90·5 camphene + 9·5 phenanthrene, $+13·5°$; (3) 65 methylthiocarbimide + 35 naphthalene, $+4·0°$. 　　T. H. P.

Inorganic Chemistry.

A New Hydrogen Table. LUDWIG VANINO and A. SCHINNER (*Zeitsch. angew. Chem.*, 1913, 26, 55—56).—The authors have con-

structed a table showing the weight of 1 c.c. of hydrogen for each degree between the temperatures 10° and 30° and for pressures of from 700 to 770 mm. The weight of 1 c.c. of hydrogen at 0° and 760 mm. is taken as 0·08995 mg.

Optical Investigation of Solidified Gases. II. Crystallographic Properties of Hydrogen and Oxygen. WALTER WAHL (*Proc. Roy. Soc.*, 1913, *A*, 88, 61—69. Compare A., 1912, ii, 1044).— The apparatus described previously has been modified so as to facilitate the investigation of the crystalline form of hydrogen and oxygen. In spite of the low temperature of crystallisation, the velocity with which hydrogen crystallises is very large. The growth structures are isotropic, and from the fact that the needle-shaped branches usually grow at right angles to a crystal face of the fully developed crystal, it is inferred that the hydrogen crystals, when fully developed, belong to one of the forms of the regular system rich in crystal faces, that is, the trisoctahedron or the hexoctahedron.

In the case of oxygen, the liquid becomes very viscous before crystallisation sets in, and the crystals which appear are badly developed, and grow very slowly. In order to obtain a homogeneous crystallised product, the cooling must take place slowly, and this condition is difficult of attainment. When the crystalline substance is further cooled it is converted into a strongly doubly-refracting, fine-grained mass of crystals, and from this it appears that oxygen is polymorphous. The transition from one form to the other takes place quite sharply, but the temperature in question has not been determined. It is, however, quite close to the melting point.

Since the physical constants of oxygen have been determined for the most part at the boiling point of hydrogen, these constants must refer to the second crystalline modification.   H. M. D.

Condensation of Water Vapour in Presence of Oxides of Nitrogen and of Hydrogen Peroxide. Evidence of the Formation of Hydrogen Peroxide by Oxidation of Water Vapour. Action of Ultra-violet Sunlight on the Earth's Atmosphere. WILLIE BIEBER (*Ann. Physik*, 1912, [iv], 39, 1313—1337).—The condensation of water vapour from dust-free gases has been examined with the view of determining the nature of the nuclei which act as condensation centres. Ozonised oxygen, which preliminary observations had shown to be free from condensation nuclei, was found to remain inactive when nitrogen was mixed with it. The admission of a small quantity of nitrogen peroxide, on the other hand, gave rise to spontaneous condensation of the water vapour, and subsequent expansion experiments showed that the nuclei formed persist for a considerable time. These observations indicate that Pringal's statement (A., 1908, ii, 798) that nitrogen is acted on by ozone in presence of water vapour, cannot be accepted.

In reference to the activity of the oxides of nitrogen, it has been supposed that nuclei are formed consisting of a higher oxide of unknown composition. Experiments with electrolytic oxygen and

oxygen prepared from hydrogen peroxide indicate that the same blue-coloured cloud is formed in oxygen which is free from nitrogen. The search for the substance which is active under these circumstances indicates that it is probably hydrogen peroxide. This is formed when ultra-violet light acts on moist oxygen, as a result of the oxidation of water vapour by the atomic oxygen, which is supposed to be produced by the action of the short waved rays on the oxygen molecules.

The formation of hydrogen peroxide by ultra-violet sunlight is considered to be chiefly responsible for the atmospheric condensation of water vapour, although nuclei resulting from the action of atomic oxygen on other constituents of the atmosphere, such as ammonia, are probably responsible for some portion of the effect.

H. M. D.

The Preparation of Anhydrous Hydrofluoric Acid and the Isolation of Fluorine. FREDERICK D. CHATTAWAY (*Chem News*, 1913, **107**, 37—39).—Historical.

Chemical Reactions at Very Low Pressures. I. The Clean-up of Oxygen in a Tungsten Lamp. IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1913, **35**, 105—127).—On heating a tungsten wire in a vacuum, a steady evolution of gas was observed. This was found to be due to water vapour given off by the glass of the bulb, which, on coming into contact with the hot wire, produced hydrogen and oxidised the tungsten. It was found that in order to avoid the formation of the gas it was necessary to heat the bulb at 360° for an hour or more after it had been exhausted, and to absorb the water vapour by means of phosphoric oxide or liquid air. By this means about 300 cubic mm. of water-vapour, 20 cubic mm. of carbon dioxide, and 4 cubic mm. of nitrogen were withdrawn from a 40-watt lamp bulb.

When a tungsten wire is heated in oxygen at a low pressure it oxidises to WO_3 at about 800° (abs.), but on raising the temperature to 1200° (abs.) the oxide volatilises, and leaves the metal clean and bright. At temperatures above 1200° (abs.) oxygen at pressures below 0·02 mm. acts on a tungsten wire at a rate which is proportional to the pressure of the oxygen and the surface of metal exposed, and increases rapidly with the temperature. No fatigue effect can be observed. The velocity is not affected by varying the temperature of the bulb. The mechanism of the reaction is discussed.

E. G.

The Presence of Selenium in Hydrochloric Acid. ENRIQUE MOLES and S. PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1913, **11**, 73—77) —It is shown that selenium probably exists in some commercial acids in the form of the dichloride, produced when seleniferous sulphuric acid is heated with salt. The presence of ferric chloride aids the formation of the selenium dichloride, although oxidising agents, such as chlorates and nitrates, do not have this effect. On diluting a seleniferous hydrochloric acid, selenium is separated as an impalpable scarlet powder.

G. D. L.

The "Chemically Active Modification" of Nitrogen. F. COMTE (*Physikal. Zeitsch.*, 1913, **14**, 74—76. Compare Strutt, A., 1912, ii, 935).—Experiments are described which seem to show that the after-luminosity effect, which is observed when a Leyden jar discharge is passed through a discharge tube containing nitrogen, is dependent on the presence of small quantities of oxygen. The apparatus used by the author was very similar to that employed by Strutt (*loc. cit.*). With nitrogen containing 0·6% oxygen, an intense orange-yellow after-luminosity was observed when the dry gas was passed through the discharge tube at a pressure of 0·5—1 mm. It is essential that the gas should be freed from water vapour, for traces of this inhibit the phenomenon. When the dry gas, before entering the discharge tube, was passed through a long tube containing copper gauze and reduced copper oxide, heated at 550°, and then over phosphoric oxide, the after-luminosity was found to disappear almost entirely when the gas had been passing through the apparatus for some time. When a small quantity of air was allowed to mix with the oxygen-free nitrogen, the luminescent effect was again obtained. The observations indicate that there is a certain small proportion of admixed oxygen which gives the maximum after-luminosity effect.

It is also shown that the passage of dry air through a discharge tube is accompanied by a similar after-luminosity if the pressure in the tube is maintained at 6 to 10 mm. of mercury.   H. M. D.

Active Nitrogen. ERICH TIEDE (*Ber.*, 1913, **46**, 340).—When pure nitrogen is used the active nitrogen of Strutt cannot be obtained. It is probable that the nitrogen used by Strutt contained oxygen, the presence of which gave rise to the observed phenomena. The matter is being further investigated in order to find the true explanation (compare also Comte, preceding abstract).
T. S. P.

Catalytic Oxidation of Ammonia. II. D. MENEGHINI (*Gazzetta*, 1913, **43**, i, 81—90. Compare A., 1912, ii, 344).—The experiments have been continued for the purpose of comparing the efficacy of different catalysts. From the results (which are shown in tables and curves) it appears that the best catalysts are roasted pyrites, chromic oxide, and a mixture of oxides of the rare earths (Nd, Pr, La); Fe_2O_3, MnO_2, and CeO_2 are less active.   R. V. S.

Chemistry of the Formation of Nitric Oxide in the High Tension Arc. ADOLF KOENIG (*Ber.*, 1913, **46**, 132—134).—The author criticises adversely the conclusions which Fischer and Heuc (this vol., ii, 132) draw from their experiments. Since active nitrogen does not react with oxygen, and ordinary nitrogen is not oxidised by ozone, it is possible that both the nitrogen and ozone are made active before combining to form nitric oxide.   T. S. P.

Chemical Reactions in Compressed Gases. Decomposition of Nitric Oxide. EMIL BRINER and BOUBNOFF (*Compt. rend.*, 1913, **156**, 228—230. Compare A., 1909, ii, 557; 1910, ii, 707; 1912, ii, 544).—A study of the decomposition of nitric oxide over wide

ranges of pressure (50 to 700 atmos.) and temperature (– 80° to 300°). Nitrogen,, nitrous and nitric oxides, and nitrogen trioxide and peroxide were found in the products of the reaction. The authors consider that two reactions take place simultaneously, namely:

(1) $2NO = N_2 + O_2$ and (2) $4NO = 2N_2O + O_2$.
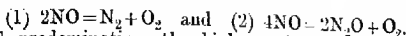
the second predominating, the higher oxides of nitrogen being produced by the secondary action of the oxygen on the untransformed nitric oxide. At constant pressure, rise of temperature accelerates the transformation and favours reaction (2) and the secondary formation of nitrogen peroxide. Increase in pressure accelerates the decomposition of the nitric oxide into more stable substances. W. G.

The **Luminescence and Ionising Action of Inactive Gases Saturated with Phosphorus Vapour.** HANS SCHMIDT (*Physikal. Zeitsch.*, 1913, **14**, 120—123).—When a current of purified hydrogen, carbon dioxide, or nitrous oxide is passed through an emulsion of phosphorus in water or through a solution in benzaldehyde, the luminosity and cloud formation, which are observed in the early stages, gradually diminish in intensity, and disappear when the oxygen has been completely removed from the apparatus. With a current of coal gas these effects vanish before the oxygen has been entirely displaced, and in this respect coal gas behaves like small quantities of ethyl ether, chloroform, ethyl alcohol, and other substances. On passing pure oxygen through the emulsion or solution, the luminosity and cloud formation disappear as the partial pressure of the oxygen rises in consequence of the removal of air.

When the inactive gases charged with phosphorus vapour are passed into the chamber of an electroscope, ionisation currents are obtained, which are very much larger than the currents obtained when air similarly saturated with phosphorus vapour is passed into the chamber. H. M. D.

The **Formation of Hypophosphoric Acid in Corne's Reaction.** FRITZ TAUCHERT (*Zeitsch. anorg. Chem.*, 1913, **79**, 350—354).—The action of yellow phosphorus on copper nitrate (Corne, A., 1882, 1264) has been investigated by Rosenheim and Pinsker (A., 1910, ii, 708), who attributed the formation of hypophosphoric acid to the action of the copper ion, and not of the nitrate ion. A comparison of other copper salts confirms this result, copper sulphate, chloride, formate, oxide, and phosphate also giving hypophosphoric acid. When phosphorus acts on copper hypophosphate, the quantity of hypophosphoric acid is also increased.

The reactions occurring are:

(1) $5Cu(NO_3)_2 + P_4 + 8H_2O = 2H_3PO_4 + Cu_3P_2 + 2Cu + 10HNO_3$.

(2) $4Cu(NO_3)_2 + P_4 + 6H_2O = H_4P_2O_6 + Cu_3P_2 + Cu + 8HNO_3$.
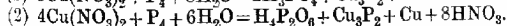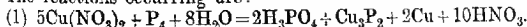
The nitric acid then reacts with the copper phosphide and excess of phosphorus, forming phosphoric and phosphorous acids and nitric oxide. Not more than 7% of the phosphorus is obtained as hypo-

phosphoric acid, whilst as much as 20% may be obtained from a hot solution of copper sulphate.   C. H. D.

The Synthesis of a Silicalcyanide and of a Felspar. J. EMERSON REYNOLDS (*Proc. Roy. Soc.*, 1913, *A*, **88**, 37—48).—In various papers (compare T., 1906, **89**, 397; 1909, **95**, 505, 508, 513, etc.) the author has given an account of organic compounds containing the silicocyanogen group, SiN, in combination, the existence of such compounds affording complete proof that silicon has a marked affinity for tervalent nitrogen. In the mineral kingdom, no definite compounds of silicon with nitrogen have been met with, but the existence of the great group of "alumino-silicates" affords clear evidence of the strong attraction of silicon for aluminium. The question therefore arises as to whether some of the alumino-silicates may not be regarded as fully oxidised products of silicides of tervalent aluminium, somewhat analogous to SiN, which have been formed at high temperatures in the first instance below the oxidised crust of the earth. Such "nuclear" silicides should be obtained either by the complete deoxidation of the corresponding native silicates, or by direct synthesis from the suitable elements. The first method has been found to be impracticable, but the second method has given satisfactory results.

The compound of silicon and aluminium analogous to cyanogen would have the formula Si_2Al_2, the name suggested for it being silicalcyanogen. Attempts to prepare this compound by synthesis from the elements were not satisfactory, combination to any material extent not taking place when a liquid mixture in atomic proportions is heated to full redness for more than two hours. It is well known that carbon and nitrogen behave similarly, but in the presence of a third element, such as an alkali metal, combination takes place with the formation of a cyanide. A mixture of silicon (103 grams), aluminium (100 grams), and calcium (74 grams), that is, in the proportion of Ca: 2Si: 2Al, behaves in an analogous manner. The silicon and aluminium are fused together, and then the calcium added in small portions at a time, the mass being stirred with a steel rod. After cooling, a dark grey, crystalline mass is obtained, the brilliant crystalline faces of a fracture apparently belonging to octahedral forms. The substance is analysed by decomposing it in a current of dry chlorine, and found to have the formula $CaSi_2Al_2$, that is, it is a *calcium silicalcyanide*, analogous to CaC_2N_2. It is readily attacked by hydrochloric acid, slowly by boiling nitric acid, and hardly at all by hot sulphuric acid. Sodium and potassium hydroxides readily decompose it. It is only very slightly attacked by oxygen until the temperature of the oxyhydrogen flame is reached, but if heated to a low redness in a stream of moist oxygen, it is converted into a white mass having a composition agreeing with that of the mineral anorthite, namely, $CaAl_2Si_2O_8$, with which mineral its physical properties are also in agreement.

Experiments in which the alkali metals were used instead of calcium gave indications of the formation of a (sodium) silical-cyanide, but pure products could not be obtained.   T. S. P.

Tschermak's Method for the Isolation of Silicic Acids. ENNIO BASCHIERI (*Jahrb. Min.*, 1912, ii, Ref. 323 ; from *Proc.-verb. Soc. Toscana Sci. Nat.*, 1910, **19**, 84—87. Compare A., 1911, ii, 502).—The following percentages of water were determined in the silicic acids isolated from apophyllite and datolite by the use of various acids of definite concentration. (The numbers given in parentheses are those in which the transformation point had been passed.)

	HCl (D 1·2).	H_2SO_4 (D 1·2).	HNO_3 (D 1·5).
Apophyllite	12·39, 12·69	12·03, (10·01)	11·33, (10·63)
Datolite............	(11·66)	12·67	13·55, 13·98

These results, as well as those obtained with some other silicates, are in close agreement with those obtained by other observers, and the correspondence can scarcely be accidental. The method is therefore of value in indicating the constitution of silicates (compare Mügge, A., 1908, ii, 277).　　　　　　　　　　　　L. J. S.

Tendency of Haloids and Phosphates of the Same Metal to Combine. II.　Alkali Fluorides and Phosphates. MARIO AMADORI (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 688—695. Compare A., 1912, ii, 940).—The present paper deals with the systems formed by the fluoride and phosphates of potassium. The melting point of potassium fluoride was found to be 855°.

In the system $KF-KPO_3$ there is evidence of the formation of the compound $2KF,KPO_3$ at 793°, and of the formation of the compound KF,KPO_3 at 880°. Mixtures containing from 0—20 mol. % of phosphate show a eutectic point corresponding with 742° and 20 mol. % of KPO_3, whilst those containing from 50—100 mol. % KPO_3 have a eutectic at 604° (82 mol. % of KPO_3). Mixtures with 0—45 mol. % of KPO_3 show a slight pause at 540°, which probably corresponds with the transformation point of the compound $2KF,KPO_3$. The transformation point (450°) of the metaphosphate is observed in all the mixtures up to 60 mol. % of potassium fluoride.

In the system $KF-K_4P_2O_7$ there is a eutectic at 730° and 20 mol. % of $K_4P_2O_7$. The transformation point (278°) of the pyrophosphate is shown by all mixtures down to 10 mol. % of $K_4P_2O_7$.

The system $KF-K_3PO_4$ has a eutectic at 766° (20 mol. % of K_3PO_4), and there is a further development of heat in the solid mass at 700°, probably due to the decomposition of a compound.
　　　　　　　　　　　　　　　　　　　　　　R. V. S.

Borates. The System $(NH_4)_2O-B_2O_3-H_2O$ at 30°. U. SBORGI (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 855—859).—The experiments were carried out by keeping mixtures of the three substances in a closed vessel in a thermostat at 30° until equilibrium was reached. Of the eleven ammonium borates which have been described, only one, namely, $(NH_4)_2O,5B_2O_3,8H_2O$, was obtained, and in addition a new *borate*, $2(NH_4)_2O,4B_2O_3,5H_2O$.

A new form of stirrer and shaker is described. A vertical axis bearing the pulley carries also a crank, and the crank-rod is a

rack, which engages with a pinion borne on a second vertical axis. The lower end of the second axis dips below the water of the thermostat, and to it the vessels to be shaken are attached symmetrically. When the pulley is revolving, the rack is moved to and fro, so that axis of the pinion makes revolutions in opposite directions alternately; this motion shakes the vessels and stirs the water of the thermostat at the same time.   R. V. S.

Silver Thioaluminates. LIVIO CAMBI (*Atti [R. Accad. Lincei*, 1912, [v], **21**, ii, 837—842).—The author has investigated the system $Ag_2S-Al_2S_3$ by the method of thermal analysis. The thermal analysis was effected in graphite crucibles in a current of hydrogen sulphide, and the composition of the mixtures was deduced by subsequent analysis. Mixtures containing more than 40 mol. % of Al_2S_3 do not yield satisfactory results. Evidence was obtained of the existence of a *compound*, $4Ag_2S,5Al_2S_3$, which melts unchanged at 1035°, and probably another compound decomposing at 825° (which is very near a eutectic point) and containing 60—70 mol. % of Ag_2S. The compound $4Ag_2S,5Al_2S_3$ forms homogeneous, flesh-coloured, birefringent crystals.   R. V. S.

Hydrates of Calcium Oxide and their Molecular Compounds. I. F. SELIVANOV (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1797—1813).—The author has studied, first, the composition of hydrates of calcium oxide prepared by slaking lime obtained by heating marble or calcium nitrate or oxalate, or by precipitating calcium chloride solution with sodium hydroxide, and, secondly, the action on these hydrates of dry water vapour.

The hydrates obtained by slaking specimens of calcium oxide of different origins all agree closely in composition with the formula $Ca(OH)_2$, whilst the precipitated hydrate contains an appreciable excess of water.

These hydrates absorb water vapour, but hold it only loosely, change of temperature from 14·5—16° to 21° resulting in a loss of almost one-third of the absorbed water. This absorbed water is largely lost in a desiccator containing heptahydrated zinc sulphate or hexahydrated calcium chloride, and is almost completely given up in presence of sulphuric acid or on heating at 60°; the last traces of the water are given up only with difficulty. Considerable differences in the proportion of absorbed water held by the hydrate are virtually without influence on the solubility in water.

From the results of his experiments the author draws the conclusion that the amorphous hydrate of calcium oxide and water behave one to the other in the same way as two liquids exhibiting slight mutual solubilities, a solution of the hydrate in water and one of water in the hydrate being formed when the two are shaken together.   T. H. P.

Solubility of the Nitrates of the Alkaline Earths in Mixtures of Alcohol and Water at 25°. JOH. D'ANS and R. SIEGLER (*Zeitsch. physikal. Chem.*, 1913, **82**, 35—44).—Mixtures of

alcohol and water of known composition are shaken with the various nitrates until equilibrium is attained, and then analysed. Three types of solubility isothermals are obtained: (1) with barium nitrate, which does not form compounds with either water or alcohol, a straight line curve is obtained, showing decreasing solubility with increasing alcohol concentration. (2) With strontium nitrate, which forms the compound $Sr(NO_3)_2,4H_2O$ with water, but does not form a compound with alcohol, a curve which is divided into two branches is obtained owing to the fact that the hydrated salt is stable in the dilute alcohol solutions, whilst the anhydrous salt is stable in the concentrated alcohol solutions. (3) With calcium nitrate, which forms $Ca(NO_3)_2,4H_2O$ with water and $Ca(NO_3)_2,2C_2H_5\cdot OH$ with alcohol, a curve of three branches is obtained. It is found that between the areas in which the hydrate and alcoholate are stable there is a small meta-stable region, in which anhydrous calcium nitrate constitutes the solid phase. The solubility of the three nitrates was also determined at 25° in methyl alcohol, ethyl alcohol, propyl alcohol, isobutyl alcohol, amyl alcohol, acetone, ether, and paracetaldehyde. Barium nitrate is found to dissolve to a slight extent only in all the solvents. Strontium nitrate is very slightly more soluble, whilst calcium nitrate is very soluble except in the cases of ether and paracetaldehyde, in which it is not more soluble than the other nitrates. J. F. S.

Action of Aqueous Barium Hydroxide on Certain Kinds of Glass. CURT BUNGE (*Zeitsch. anal. Chem.*, 1913, **52**, 15—17).— An insoluble coating observed in a burette in which $N/4$-barium hydroxide had been kept was found to consist of barium sulphate.

Further investigation proved the sulphate to be derived from the glass, and evidently owing to the use of sodium sulphate in glass manufacture. L. DE K.

The Solubility of Glucinum Sulphate in Water and Sulphuric Acid. FRITZ WIRTH (*Zeitsch. anorg. Chem.*, 1913, **79**, 357—359. Compare Parsons, A., 1904, ii, 658; 1905, ii, 34; Levi-Malvano, A., 1906, ii, 165).—The solubility of glucinum sulphate hexahydrate in water at 25° is much less than that previously recorded, being only 0·07857 mol. in 100 grams of solution. Sulphuric acid at first only slightly lowers the solubility, but beyond 12·5N the hexahydrate passes into the tetrahydrate, the solubility of which is much further diminished by sulphuric acid. As the solubility curve of aluminium sulphate in sulphuric acid has an entirely different form, this property may be used for the purification of glucinum salts. C. H. D.

Glucinum Chromates. N. A. ORLOV (*Zeitsch. anorg. Chem.*, 1913, **79**, 365—367. Compare Bleyer and Moormann, A., 1912, ii, 762). —The following compounds have been obtained: from glucinum sulphate and potassium chromate, $9GlO,GlCrO_4,16H_2O$ and $20H_2O$ and $14GlO,GlCrO_4,31H_2O$; from a solution of glucinum hydroxide in chromic acid and potassium chromate, $12GlO,GlCrO_4,16H_2O$; and

by precipitating a solution of glucinum hydroxide in chromic acid with alcohol, $5GlO,GlCrO_4,14H_2O$. Glucinum and aluminium chromates are gradually hydrolysed by water, without the formation of any definite basic salt.   C. H. D.

The Thermal Dissociation of Amorphous Magnesite. O. KALLAUNER (*Chem. Zeit*, 1913. **37**, 182). — Amorphous magnesite begins to lose carbon dioxide at 500°, but the temperature at which the evolution takes place almost momentarily is 620—625°.

. T. S. P.

Action of Hydrogen Peroxide on Alkaline Solutions of Lead Oxide. V. ZOTIER (*Bull. Soc. chim.*, 1913, [iv]. **13**, 61—66). — In this reaction lead peroxide is first formed, which then reacts with some hydrogen peroxide, giving rise to oxygen and some lead oxide, so that the precipitate produced usually consists of both oxides.

With increasing quantities of hydrogen peroxide, the quantity of lead peroxide rises to a maximum, and then remains constant. For the quantity of hydrogen peroxide necessary to produce this maximum quantity of lead peroxide, the reaction is expressed by the equation $10PbO + 10H_2O_2 = 10H_2O + 4PbO_2 + 6PbO + 3O_2$.

The amount of lead peroxide formed diminishes with rise of temperature, slightly up to 30°, considerably from 30° to 60°, and very rapidly above 60°. About 90—95°, lead peroxide is formed, but disappears immediately, due to the second phase of the reaction.

Water has little influence on the reaction, and considerable quantities must be introduced before differences greater than those due to experimental error are noticeable.

The quantity of lead peroxide formed diminishes as the ratio NaOH : PbO increases, and with sufficient sodium hydroxide the lead peroxide formed is immediately decomposed.   T. A. H.

Tendency of Haloids and Phosphates of the Same Metal to Combine. III.   Fluoride, Chloride, and Phosphate of Lead. MARIO AMADORI (*Atti R Accad. Lincei*, 1912, [v], **21**, ii. 768—774. Compare this vol., ii, 213).—Lead orthophosphate has m. p. 1006°, and its cooling curve shows a transformation point at 782°. Mixtures of lead orthophosphate and lead fluoride, containing from 0 to 10 mol. % of phosphate, show a eutectic corresponding with 678° and 7·5 mol. % of phosphate. The curve also shows a maximum at 1046° and 75 mol. % of phosphate, and at this temperature the compound of the same composition, $PbF_2,3Pb_3(PO_4)_2$, crystallises. The eutectic pause is not seen in mixtures containing more than 10 mol. % of phosphate. The curve of the compound $PbF_2,3Pb_3(PO_4)_2$ shows a transformation point at 696°, and it probably exists also in a third modification. There is complete miscibility between the α-form of the compound and the α-form of the phosphate, and there is extensive solubility in the solid state between the α-form of the compound and the fluoride. Between the presumed β-form of the compound and the β-form of the phosphate there is also probably complete miscibility, whilst this

modification of the compound and the fluoride probably form a series of mixed crystals. The γ-form of the compound is not miscible (or is miscible only to a very limited extent) with the β-form of the phosphate, and it is not miscible with the fluoride.

Owing to the volatility of the chloride, the experiments with lead chloride and lead orthophosphate were mainly qualitative, but it is probable that a compound is formed analogous to that above described; its m. p. lies above 1100°.

The compound of fluoride and phosphate corresponds with calcium salts (apatite) occurring in nature, and that between chloride and phosphate would correspond with pyromorphite.

R. V. S.

Double Salts of Thallous Chloride with Ferric Chloride and with Bismuth Chloride. G. Scarpa (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 719—725).—The paper gives an account of the thermal analysis of the systems $TlCl–FeCl_3$ and $TlCl–BiCl_3$.

In the case of the former system the volatility of ferric chloride causes some experimental difficulties, and it is necessary to determine the composition of the mixtures by actual analysis of the separated solid. For the same reason, it is not possible to deal with mixtures containing more than 62 mol. % of ferric chloride. There is a eutectic corresponding with 266° and 26 mol. % of ferric chloride, and a maximum at about 33 mol. % of ferric chloride and 290°. This indicates the formation of a compound $2TlCl,FeCl_3$, stable on fusion. Mixtures containing more ferric chloride show a eutectic point at about 220°, and the initiation of crystallisation is very high; for instance, the mixture with 62% of ferric chloride begins to crystallise at 299°, which is almost the m. p. of ferric chloride. It is therefore legitimate to suppose that the curve would show another maximum above this point.

In the system $TlCl–BiCl_3$, there is a eutectic corresponding with 360° and 12·5 mol. % of bismuth chloride, and a maximum at 413° (25 mol. % of bismuth chloride). A pause occurs at 330° (about 40 mol. % of bismuth chloride), and a more evident pause at about 225° (52 mol. % of bismuth chloride). The curve then descends to a eutectic at 150° (67 mol. % of bismuth chloride), and finally rises to the m. p. of this salt. Mixtures containing 0—25 mol. % of bismuth chloride show a pause at 360°, which vanishes for the 25% mixture; this indicates the existence of the compound $3TlCl,BiCl_3$. Mixtures from 25% to 40% of bismuth chloride exhibit a slight pause at 330°, probably due to the formation of a compound $2TlCl,BiCl_3$, which decomposes on fusion. Mixtures containing 35—50 mol. % of bismuth chloride show a pause at 224°, which demonstrates the existence of a compound $3TlCl,2BiCl_3$, decomposing on fusion. Above 70% of $BiCl_3$, the mixtures deposit mixed crystals.   R. V. S.

Molecular Complexity of Metals in the Solid Phase. Maurizio Padoa and F. Bovini (*Atti R. Accad. Lincei*, 1912, [v]. **21**, ii, 708—713).—From the diagram of the system copper bismuth, which is known, the authors calculate the cryoscopic constant of

copper (874·5) in good agreement with the value obtained from the heat of fusion of copper (855). Mixtures of copper and silicon containing little silicon are simple solutions of the silicon in the copper, and applying the above constant, the authors calculate (from published data of this binary system) the molecular weight of silicon dissolved in liquid copper. The values obtained vary from 32·7 to 24·5, indicating that in these circumstances silicon is monatomic. It is probable that its state of aggregation is the same also in solution in solid copper.

[With CARLO MARANI.]—The authors have also determined the molecular complexity of cadmium in solution in solid tin. In the system Sn–Cd–Bi, bismuth does not form solid solutions with either of the other constituents, whilst cadmium gives a solid solution with tin. Analysis of the crystals separating from the solution of cadmium in tin (bismuth being also present) shows that the solid solution has very nearly the same composition as the liquid solution, the partition coefficient being sensibly constant, and therefore the cadmium has the same degree of molecular complexity in both, that is, it is monatomic also in the solid solution. R. V. S.

Electrical Conductivity of Alloys of Copper and Zinc. NIKOLAI A. PUSCHIN and V. N. RJASHSKI (*J. Russ. Phys. Chem. Soc.,* 1912, **44**, 1905—1918).—Investigation of the electrical resistance and of its temperature-coefficient for alloys of copper and zinc gives results in general agreement with Shepherd's conclusions based on the melting-point diagram and on the microstructure (A., 1904, ii, 662). The system forms (1) the solid solutions: a, 0—36 atom %; γ, 59—67 atom %; ϵ, 80—85·7 atom %; and η, 91—100 atom % of zinc; (2) the mixed crystals: $a + \beta$, 36—50; $\beta + \gamma$, 50—59; $\gamma + \epsilon$, 67—80; and $\epsilon + \eta$, 85·7—91 atom % of zinc. The existence of the solid solution, β, within narrow limits is regarded as a sign of the existence of the definite compound ZnCu, which is slightly dissociated at the ordinary temperature. The results also indicate the probable existence of the two compounds, Zn_2Cu and Zn_6Cu (compare also Norsa, A., 1912, ii, 890). T. H. P.

The Tensile Strength of the Copper–Zinc Alloys. J. M. LOHR (*J. Physical Chem.,* 1913, **17**, 1—25).—The brasses examined covered the whole range of useful mixtures, namely, from 47·5% to 100% of copper. The metals were melted under coal gas and poured from a plug hole in the bottom of the crucible in order to avoid dross. The pouring temperatures by thermocouple were from 50° to 250° above the liquidus points. The mould consisted of a split Acheson graphite block arranged to cast a test-bar 6 in. long, by 0·40 in. diameter, with an S-shaped gate termed a "centrifugal sprew" and a very substantial riser, the test-bar being slightly inclined so as to sweep forward and upward into the riser any floating zinc oxide. The mould was preheated by external gas burners. With these precautions test-bars were usually obtained free from blow holes and dross. Any bar which showed signs under a lens of pipe formation or pinholing after fracture was rejected.

After casting, the bars were quickly removed from the mould

and chilled in water from a temperature of 700—800°, and were subjected to no other heat treatment before testing. Consequently they consisted of pure α-phase down to 66% of copper, mixed α- and β-crystals from 66% to 57% of copper, pure β-crystals from 57% to 50%, and mixed β- and γ-crystals below 50%. Owing to the high temperature of quenching, α- and γ-mixtures were not present, and in the range of compositions studied, pure γ-, as well as the δ-, ε-, and η-phases do not exist.

The α-brasses have a tensile strength which is almost constant at about 33,000 lb. per sq. in. from 95% to 66% of copper. When the β-phase appears, the strength rises and attains a maximum at 55% in the pure β-phase of about 71,000 lb., or when calculated on the reduced area, 100,000 lb. per sq. in., with an elongation of 14·8%. The strength falls off rapidly when the γ-phase appears, the 47·5% copper alloy, which appeared to contain about three-fourths β-crystals with one-fourth γ-crystals, giving 23,000 lb. only.

The maximum elongation of 36% was observed in the α-phase at 62% to 70% of copper, the corresponding tensile strength being 36,000 lb. Occasional specimens gave higher results; for example, in one case, the elongation was 60%, and in another the tensile strength 137,000 lb. per sq. in.

It was noticed in casting that alloys between 100% and 80% of copper and between 65% and 47·5% of copper usually gave homogeneous test-pieces, whereas between 80% and 65% of copper (maximum ductility), it was difficult to obtain castings free from porosity. The best pouring temperature was from 100° to 200° above the liquidus. Below this the metal was usually too viscous, and above this it often contained black spots of porous material.

R. J. C.

Some Basic Copper Sulphates. GEORGE FOWLES (*J. Soc. Chem. Ind.*, 1913, **32**, 9).—The author points out that some of the results published by Ermen (A., 1912, ii, 453) have been obtained previously by other investigators.　　　T. S. P.

Blue Gelatin Copper. WILDER D. BANCROFT and T. R. BRIGGS (*J. Ind. Eng. Chem.*, 1913, **5**, 9—11).—One gram of gelatin is dissolved in 325 c.c. of a 1% solution of cupric acetate, and the solution electrolysed for five minutes between carefully cleaned and burnished electrodes of sheet copper, using a current density of 0·15—0·45 amps. per sq. dcm. at the cathode. The cathode becomes covered with a thin, pale brown deposit, possessing a peculiar, slippery surface, owing to the gelatin deposited with the copper. If the cathode is washed, and then immersed in a 5% solution of copper acetate containing no gelatin, a series of remarkable colour changes takes place until the surface has acquired a magnificent deep blue coloration. The process of the formation of this blue colour is called "development" by the authors.

Gelatin, in concentrations varying from 0·25 to 0·66%, must be present for development to occur. The copper acetate may be replaced by copper propionate or formate (not so good), but not by

the sulphate, nitrate, or chloride. The most satisfactory temperatures lie between 20° and 40°; at 50° or higher temperatures, red or golden films are produced, which will not develop, but may be preserved by 'lacquering. The copper acetate or propionate solution should contain 1 or 2 parts of the crystallised salt to 100 parts of water; the limits of current density are given above. Anodes of nickel, brass, or platinum may be used.

Experiments with various solutions showed that development takes place successfully only in solutions of copper acetate or propionate, so that this phenomenon must be a function of the copper contained in the developing solutions. If the developed electrode is placed in a solution of hydrazine hydrate, the colour slowly disappears, with evolution of nitrogen; it may then be re-developed, but not to such a good colour as before, in copper acetate solution. If the deposited film is left undeveloped for several hours, it completely loses its power of developing in copper acetate, probably because of oxidation.

The deposited film of metal is probably an irreversible gel of colloidal copper, and the process of development is an adsorption of hydrated copper oxide by the surface of the colloid film. This hydrated copper oxide is present as a suspension in very appreciable quantities in the acetate or propionate solutions.   T. S. P.

Action of Distilled Water on Impure Aluminium. ALBERTO SCALA (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 43—49) —When ordinary aluminium (Kahlbaum) is kept in contact with carefully prepared distilled water at the ordinary temperature it eventually shows signs of chemical action, for the surface becomes black, and bubbles of gas appear. The time elapsing before this action is evident varies from months to days in different experiments, but when once started it proceeds somewhat rapidly. Suspended in the water are then to be found aluminium hydroxide and a chestnut-coloured substance, which is a compound containing aluminium, iron, and perhaps silicon. During the reaction hydrogen is evolved.

R. V. S.

Alloys of Aluminium and Vanadium. NICOLAS CZAKO (*Compt. rend.*, 1913, **156**. 140—142. Compare Moissan, A., 1896, ii, 608; Matignon and Monnet, A., 1902, ii, 326).—By fusing vanadic acid with aluminium in the necessary proportions, the author has prepared alloys of aluminium and vanadium, containing from 1 to 80% of vanadium, and has examined them micrographically. He has isolated crystals having the definite constitution Al_3V and AlV, and obtained indications of a compound AlV_2. The hardness of the alloys increases with the vanadium content up to 60%, when it is from 6 to 7, after which it diminishes. The alloy containing 53% vanadium is full of cavities, and in consequence difficult to examine micrographically.   W. G.

The Crystallisation of Pure Aluminium Salts from Solutions containing Iron, and the Artificial Preparation of Halotrichite. FRITZ WIRTH (*Zeitsch. angew. Chem.*, 1913. **26**. 81—83).—The author has determined the solubilities at 25° of

ferrous sulphate, aluminium sulphate, and of each of these salts in the presence of, varying proportions of the other. in order to determine the region of the existence of the double salt, halotrichite, $FeSO_4,Al_2(SO_4)_3,24H_2O$. The solubilities of the pure components are respectively 0·8124 mol. of aluminium sulphate, and 1·503 mols. of ferrous sulphate in 1000 grams of solution. The double salt exists over the region between the two solutions containing respectively 0·723 mol. of aluminium sulphate and 0·38 mol. of ferrous sulphate, and 0·7045 mol. of aluminium sulphate and 0·6827 mol. of ferrous sulphate. It follows that from a solution containing equimolecular quantities of the two salts, ferrous sulphate first crystallises, and then the double salt. The preparation of the double salt is best carried out by shaking a solution, saturated with respect to the two components, with the solid sulphates contained in a silk bag. Strongly supersaturated solutions are thus obtained, from which the double salt separates after a few hours.

The solubility curve gives the conditions of relative concentrations under which pure aluminium sulphate can be crystallised out from a solution containing ferrous sulphate, and experiments made by the author show that complete separation of aluminium from iron can thus be carried out. If the iron is in the ferric condition, separation is impossible, owing to the formation of mixed crystals; the iron must first be reduced to the ferrous state. A method is thus given, which is applicable commercially, for the preparation of pure aluminium sulphate from bauxite.　　　　　T. S. P.

The Solubility of Aluminium and Iron Sulphates in Sulphuric Acid. FRITZ WIRTH (*Zeitsch. anorg. Chem.*, 1913, **79**, 360—364).—The presence of sulphuric acid at first increases the solubility of aluminium sulphate in water, but a further addition of acid produces an enormous depression. From $20N$ onwards there is again a slight increase, without any change in the solid phase. This has already been observed with other sulphates. With concentrated sulphuric acid, aluminium sulphate forms the compound $Al_2(SO_4)_3,H_2SO_4,3H_2O$, the mixture solidifying after a few hours.

Ferrous sulphate is converted into the monohydrate by sulphuric acid of greater concentration than $12·5N$ at $25°$. The solubility curve of ferrous sulphate in sulphuric acid is nearly parallel to that of aluminium sulphate as far as 40% H_2SO_4. Ferric sulphate is somewhat less soluble.　　　　　C. H. D.

Ultramarine Compounds. II. L. WUNDER (*Zeitsch. anorg. Chem.*, 1913, **79**, 343—349. Compare this vol., ii, 54).—When ultramarine red is heated out of contact with air, it is converted into a blue product, the loss of weight which occurs being due to loss of water. The constitution is, however, changed, as the new blue evolves hydrogen sulphide with acids, whilst the red yields sulphur dioxide. It differs from commercial ultramarine blue in not being converted into violet by heating in chlorine and hydrogen chloride at 170—250°, and in not being reduced to white by the action of phosphorus in carbon tetrachloride. In accordance with

its higher proportion of silica, the new blue is more stable towards acids and alum than ordinary ultramarine.

The presence of the sodium is necessary for the blue colour, complete replacement by mercury yielding a yellow product. The violet ultramarine yields a yellow silver derivative, which again becomes violet when heated with lithium chloride. The silver derivative of ultramarine red is brown, and is free from sodium. Alkali haloids convert it into blue.

The blue colour is considered to depend on (1) the presence of an alkali metal, (2) the direct union of a part of the sulphur with metal, (3) the presence of a part of the sulphur in a lower state of oxidation. Neither aluminium nor silicic acid is essential, as the former may be replaced by boron, and the latter by a polyboric acid. Boron-ultramarine, however, fulfils the conditions mentioned above (compare Hoffmann, A., 1906, ii, 545). The colloidal theory of the blue colour is rejected.   C. H. D.

The Heusler Ferromagnetic Manganese Alloys. EDGAR WEDEKIND (*Zeitsch. angew. Chem.*, 1913, **26**, 72).—Polemical. A reply to Heusler (this vol., ii, 139).   L. DE K.

The Reactions which Accompany the Osmosis of Hydrogen through Iron. GEORGES CHARPY and S. BONNEROT (*Compt. rend.*, 1913, **156**, 394—396. Compare A., 1912, ii, 336).—A study of the change in iron and steel when submitted to the prolonged diffusion of hydrogen through it at 600—900°. Iron thus traversed for a long time by a current of hydrogen does not absorb any of the gas, since the amount of hydrogen obtainable on heating the iron in a vacuum is generally slightly less after than before the osmosis. The physical properties of the metal are modified, it being softened by prolonged diffusion of the gas, which exercises a reducing action, removing such constituents as sulphur, phosphorus, and carbon in the form of their hydrides, the desulphurisation being particularly rapid. In an experiment on a steel tube, 3·5 mm. thick, containing 0·9% carbon, at 900°, 2·3 c.c. of gas diffused through, and was found to contain 4% of hydrocarbons. The iron thus undergoes a process of purification by the passage of the hydrogen, and this may possibly explain certain of the anomalies in the metallurgy of iron and steel, the hydrogen arising from the contact of water vapour with the hot metal.   W. G.

The Transformations of Iron and Steel at High Temperatures. KÔTARÔ HONDA and HIROMU TAKAGI (*Sci. Reports, Tôhoku Imp. Univ.*, 1912, **1**, 207—217).—A series of specimens ranging from pure iron to steel containing 1·50% of carbon have been examined in an electric furnace by a magnetometric method, simultaneous observations of time, temperature and magnetic deflection being made.

The β–α magnetic transformation extends over a small interval of temperature. The interval β–α or γ–α increases with increasing carbon in steels, as measured magnetically, whilst the thermal

change is not recognisable. The eutectoid point is marked by an increase in the magnetic properties on cooling.   C. H. D.

The System Iron–Carbon. OTTO RUFF (*Zeitsch. Elektrochem.*, 1913, **19**, 133).—Polemical. An answer to Smits (this vol., ii, 56). The author states that Smits bases his calculations on experiments which are only to be regarded as preliminary.   J. F. S.

Complete Solubility of Chromium Hydroxide in Ammonia. MILORAD Z. JOVITSCHITSOH (*Monatsh.*, 1913, **34**, 225 — 242).— Chromium may be precipitated with small quantities of ammonium hydroxide as a light grey hydroxide which dissolves in excess with ruby-red colour, the solubility being influenced by salts of ammonium. From the solution substances may be obtained which contain hydroxyl groups, ammonia, and, according to circumstances, acid radicles. They are not to be considered as derivatives of normal chromium hydroxide, $Cr_2(OH)_6,4H_2O$, as, for example, $(NH_3)_8Cr_2(OH)_2Cl,4H_2O$, but rather as based on Colson's hypothetical oxyhydroxide (A., 1908, ii, 45), with which the analyses and properties are most in accordance.

The solution of chromium hydroxide may be effected in different ways, but the best consists in dissolving 1 gram of the substance in just sufficient mineral acid, diluting to about 25 c.c., and adding the same volume of ammonia. A grey precipitate is formed, which redissolves in the course of an hour or so. *Tetrachromiumoxide-*

hexamminodisulphate, $\begin{array}{c}(NH_3)_2{:}Cr{\cdot}O{\cdot}NH_3{\cdot}Cr{:}SO_4\\(NH_3)_2{:}Cr{\cdot}O{\cdot}NH_3{\cdot}Cr{:}SO_4\end{array},10H_2O$, is precipitated

by alcohol from such a solution as a red oil which, when freed from ammonium sulphate, solidifies to a red mass. When dried over sulphuric acid, it loses $4H_2O$, but when left in contact with water, it gradually suffers hydrolysis and becomes paler, the acid radicles being partly replaced by hydroxyl groups. It is stable in absolute alcohol, but absorbs carbon dioxide when exposed to the air. The addition of alcohol to the solution made with nitric acid at first causes the precipitation of a pale pink amminochromium hydroxide, but later on, *tetrachromiumoxide-*

heptamminotrinitrate, $\begin{array}{c}(NH_3)_2Cr{\cdot}O{\cdot}NH_3{\cdot}Cr(NO_3)_2\\(NH_3)_2Cr{\cdot}O{\cdot}NH_3{\cdot}Cr{<}^{NO_3}_{NH_3}\end{array},10H_2O$, separates as

a scarlet, dense mass, which is soluble in water, but is speedily hydrolysed. The preparation of *tetrachromiumoxidehexamminodi-*

chloride, $\begin{array}{c}(NH_3)_2Cr{\cdot}O{\cdot}Cr(NH_3)_2\\(NH_3)_2Cr{\cdot}O{\cdot}CrCl_2\end{array},10H_2O$, as a violet-red precipitate

is even more difficult. It is soluble in water, but only after some hours does silver nitrate form a precipitate. No change is observed when the ruby-red solutions are neutralised, but when they are kept, *diamminochromium hydroxide,*

$$Cr(OH)_6(NH_3)_2,10H_2O,$$

is precipitated as a violet-blue mass which absorbs carbon dioxide.
     J. C. W.

Diffusion of Molybdenum in the Coalfield of Liège.
ARMAND JORISSEN (*Bull. Soc. chim. Belg.*, 1913, **27**, 21—25. Compare
A., 1897, ii, 265).—The author has examined samples of soot and
fine dust resulting from the combustion of coal from this district,
and has succeeded in isolating molybdenum in small quantities
therefrom in the form of its sulphide, and has further identified
it by the characteristic tests. A portion of the molybdenum is
present in a form soluble in and extracted by water.   W. G.

**Iso- and Hetero-Poly-salts. VII. Molybdic Acid Hydrates
and Some Polymolybdates.** ARTHUR ROSENHEIM and JOSUA FELIX
[with JACOB PINSKER] (*Zeitsch. anorg. Chem.*, 1913, **79**, 292—304.
Compare A., 1911, ii, 116; Wempe, this vol., ii, 58).—Octo-
molybdates are prepared by adding the calculated quantity of
hydrochloric acid to normal molybdates, or by saturating solutions
of the latter with molybdic acid dihydrate. The salts have the
formula $M'_2Mo_8O_{25}$, the calcium and barium salts having $18H_2O$,
the sodium salt $17H_2O$, the ammonium salt $16H_2O$, and the
potassium salt $13H_2O$. Sodium octamolybdate passes at the
ordinary temperature into a decamolybdate, $Na_2Mo_{10}O_{31},6H_2O$.

The electrical conductivity of the aqueous solutions shows that
the octamolybdates contain ionisable hydrogen. They are therefore
hydrogen tetramolybdates, such as $NaHMo_4O_{13}$, and when neu-
tralised yield normal tetramolybdates, such as $Na_2Mo_4O_{13}$, the
electrical conductivity of which shows that they are entirely similar
to the metatungstates.

The tetramolybdates are thus 12-molybdic acid hydrates,
$M'_6H_4[H_2(Mo_2O_7)_6]$, and the octamolybdates are hydrogen salts with
the same complex anion, $M'_3H_7[H_2(Mo_2O_7)_6]$.

Sodium tetramolybdate, $Na_6H_4[H_2(Mo_2O_7)_6],21H_2O$, forms micro-
scopic, yellow crystals. The *potassium* salt has $18H_2O$, the *barium*
salt $12H_2O$, the *guanidinium* salt, like the corresponding meta-
tungstate is anhydrous. The octamolybdates already known are
formulated afresh in accordance with this view of their constitution.

Two series of decamolybdates exist, one readily, and the other
sparingly, soluble, and either isomeric or polymeric. When a
soluble salt is added to hot water, it dissolves immediately, but if
warmed with an insufficient quantity of water, it passes into the
sparingly soluble modification. The following salts have been
prepared: (soluble) $(NH_4)_2Mo_{10}O_{31},19H_2O$; $K_2Mo_{10}O_{31},15H_2O$;
$Na_2Mo_{10}O_{31},22H_2O$; (sparingly soluble) $(NH_4)_2Mo_{10}O_{31}.3H_2O$;
$K_2Mo_{10}O_{31},9H_2O$.

It has not been found practicable to prepare the free acid.
C. H. D.

Uranyl Iodates. PAUL ARTMANN (*Zeitsch. anorg. Chem.*, 1913. 79.
327—342).—Uranyl iodate has been described with $5H_2O$, with
H_2O, and anhydrous. It is now found that the precipitation of
uranyl nitrate solution with sodium iodate yields a salt with H_2O
or $2H_2O$, according to the conditions. The monohydrate forms

rhombic prisms when precipitated from cold solution, or pyramids from hot solution. The two modifications have D^{18} 5·220 and D^{18} 5·052 respectively. The first is converted into the second by boiling, whilst the reverse transformation occurs slowly at the ordinary temperature.

The dihydrate has a lighter yellow colour, and forms irregular aggregates.

Uranyl potassium iodate, $UO_2K(IO_3)_3,3H_2O$, is a very sparingly soluble yellow powder, and is obtained by precipitation with an excess of potassium iodate. It is hydrolysed by water, and is converted into uranyl iodate by an excess of uranyl nitrate.

Uranyl iodate does not give up its last mol. of water when heated. It is assumed to have the constitution:

$$OH \cdot UO_2 \cdot O \cdot IO \ll_O^O \gg IO \cdot OH,$$
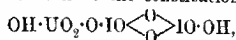
the anhydrous potassium salt being $IO_3 \cdot UO_2 \cdot O \cdot IO \ll_O^O \gg IO \cdot OK.$

C. H. D.

Zirconium. II. EDGAR WEDEKIND (*Annalen*, 1913, 395, 149—194. Compare A., 1910, ii, 302).—[With HANS KRŽEL.]— The preparation of the metal by the reduction of the oxide by the Goldschmidt process fails in the case of zirconium, as also of other highly infusible metals. Reduction of the oxide by magnesium also is unsatisfactory. The following process of reduction by calcium, however, is convenient, and gives good results.

An intimate mixture of zirconium oxide and an excess of the finest calcium shavings is heated in an iron tube under a pressure of 0·1—0·5 mm., the heating being discontinued as soon as the reaction commences. When quite cold, the contents of the tube are powdered, and are treated successively with cold water, acetic acid, dilute hydrochloric acid, and water (until the washings do not contain calcium chloride), all of these operations being performed in the absence of air. The residual powder is finally washed with acetone and dried at first at the ordinary temperature, then in a high vacuum at 250—300°, and finally in a completely evacuated porcelain tube at 800—1000°. At the last temperature, which is far below the m. p. of zirconium, the powder sinters to lumps, which exhibit the brilliancy of a mirror by polishing. The metal obtained in this manner contains 99·09% of zirconium. An attempt to remove the small quantity of oxygen still present, by heating again with calcium in a nickel tube, resulted in the isolation of a less pure product. The yield of the powder is 97·5%; it has D^{18} 5·98, the sintered modification having D^{11} 6·280 and $D^{17·5}$ 6·204. When pressed into rods and fused electrically in a vacuum (compare Weiss and Neumann, A., 1910, ii, 217), the powder is converted into globules, D^{16} 6·40, containing 98·5% of zirconium, being therefore less pure than the globules obtained by Weiss and Neumann (*loc. cit.*).

Titanium, thorium, uranium, vanadium, and tantalum have also been prepared by the calcium method.

The m. p. of zirconium is given as about 2350° by Wedekind and Bolton (A., 1910, ii, 302). Estimations by Burgess's platinum method (A., 1909, ii, 41) give a mean value, 1530°, of the m. p. The latter value is probably more correct, since zirconium cannot be employed for the manufacture of metal filament lamps.

Weiss and Neumann (*loc. cit.*) have described a zirconium hydride, ZrH_2. If this is a chemical individual, it is of great interest as being the first authentic example of a derivative of bivalent zirconium. The authors have also prepared this substance by heating zirconium powder in hydrogen at 700° and 1·5 atmospheres, and are of opinion that it is a chemical individual of the formula ZrH_2; its dissociation pressure at temperatures up to 1100° has been measured. Evidence of the existence of a volatile zirconium hydride has not been obtained.

In contrast to titanium, zirconium and nitrogen do not react much at temperatures below 1000°, but at 1000—1050°, a *nitride*, Zr_3N_2, D^{15} 6·75, a microcrystalline, tombac-coloured, glistening powder, is formed. The nitride is more stable than zirconium towards oxygen or chlorine, dissolves readily only in hydrofluoric acid, and is stable to aqueous alkalis. Fused potassium hydroxide or sodium carbonate causes an incomplete evolution of the nitrogen as ammonia. The nitride has no measurable dissociation pressure at 1100°, and in the compressed state is a conductor of electricity. The nitride, which is also produced by heating zirconium in ammonia at 1000°, partly loses its nitrogen by heating in hydrogen at 1050°; a partial formation of the nitride is also observed when zirconium hydride is heated in nitrogen at 1050°.

[With S. JUDD LEWIS.]—According to the literature, zirconium has been prepared in crystalline, graphitic, and amorphous modifications. It has already been shown that "crystalline zirconium" is an aluminium zirconide. The existence of Troost's graphitic zirconium, prepared by heating iron and sodium zirconate, is more than doubtful, since a reduction of zirconium oxide by iron is impossible. The black, amorphous zirconium prepared by Berzelius by heating potassium zirconium fluoride and potassium, has also been prepared by the authors (a better result is attained by using sodium instead of potassium), and found not to be an individual substance. It has the characteristics of a gel, and retains water most pertinaciously. By treatment with acids, it is converted into the hydrosol, from which the gel is recovered by coagulation or by evaporation after dialysis.

Amorphous zirconium and its gel are very closely related. The latter contains more oxygen and an appreciable amount of nitrogen. It has D^{16} 3·75, but the higher the temperature at which the amorphous zirconium or its gel is dried, the greater is the density, until, after drying at about 1000° in a high vacuum, it has D^{21} 5·79. Compressed amorphous zirconium or its gel is a nonconductor of electricity at low voltages, but becomes a conductor after being heated at 1000° in a vacuum. In its chemical properties, amorphous zirconium or its gel behaves very like metallic zirconium. It burns brilliantly when gently heated, is very stable

towards dilute acids, and is slowly attacked by chlorine. It inflames when heated with sulphur, and yields a mixture of the oxide and sulphide; with selenium a greyish-black *selenide* is produced. Reasons are given for the belief that amorphous zirconium is not a mixture of finely divided metal and the dioxide, or of the metal and the monoxide.

The authors are of opinion that amorphous zirconium is the colloidal modification of the metal. By treatment with acids, it yields the hydrosol. The gel recovered from the latter by coagulation agrees in its properties with the amorphous zirconium prepared directly by Berzelius's method. The two modifications of zirconium bear to one another the same relation as do amorphous and crystalline silicon.

|With J. TELETOW.]—Zirconium dioxide has been reduced by magnesium in hydrogen at high temperatures, whereby about one-third of the oxide escapes reduction. By a second and a third repetition of the reduction, the product becomes more and more pyrophoric and unmanageable, but in no case has the amount of zirconium corresponded with that required by a zirconium oxide, ZrO, the existence of which has been assumed by Winkler and by Dennis and Spencer (*J. Amer. Chem. Soc.*, 1896, 18, 651). C. S.

The Subhaloid Compounds of Some Elements. I. The So-called Bismuth Subiodide. Luioi MARINO aod R. BECARELLI (*Atti R. Accad. Lincei*, 1912, [v]. 21, ii, 695—701).—The authors have investigated the system Bi–I by the method of thermal analysis, and find no iudication of the existence of any compound of the two elements other than BiI_3. The heating and subsequent cooling of the mixture of the two elements were effected in a sealed glass tube, precautions being taken to exclude all traces of water. The eutectic of Bi and BiI_3 lies at 284°. When mixtures containing 5—43% of iodine are cooled, two layers are formed, of which the upper contains excess of BiI_3, and the lower excess of Bi. At 340° the upper layer begins to deposit solid BiI_3, and as an invariant system is thus formed, this crystallisation continues until all the upper has solidified; during this process the upper layer contains 66·5% of BiI_3, aud the lower 7·73%. Mixtures with 43--64·63% of iodine deposit BiI_3 until the temperature 340° is reached; two layers are then formed as before. After the upper layer has crystallised, the temperature falls until the eutectic 284° is reached, but there is a thermal effect at 294°, possibly due to a transformation product of bismuth. Mixtures containing more thau 64·63% of iodine deposit BiI_3, aud show a eutectic at 117°, but mixtures with more thau 90% of iodine could not be investigated, owing to the breakage of the tubes in consequence of the pressure of the iodine vapour.
　　　　　　　　　　　　　　　　　　　　　R. V. S.

History of Colloidal Gold. I. Gold Ruby Glass. ALFONSO CORNEJO (*Zettsch. Chem. Ind. Kolloide*, 1913, 12, 1—6).—The view that Kunckel (1679) was the original discoverer of ruby gold glass is erroneous, for Libavius (1595), Neri (1614), Glauber (1648),

Cassius, and Tachenius (1668) not only employed gold as a colouring agent, but gave exact directions, for the preparation of ruby gold glass.   H. M. D.

Disintegration of Metals at High Temperatures. Condensation Nuclei from Hot Wires. JOSEPH H. T. ROBERTS (*Phil. Mag.*, 1913, [vi], **25**, 270—296. Compare Crookes, A., 1912, ii, 563).—The disintegration of the platinum metals at high temperatures has been investigated, the formation of clouds in a Wilson expansion apparatus being employed as a delicate means of detecting the presence of disintegrated particles in the gaseous atmosphere surrounding the electrically heated metal wires. As evidence of the superiority of this method of investigating the disintegration, it is stated that no loss of weight could be detected on heating a platinum wire for thirteen hours at 650°, whereas a dense cloud was obtained in the expansion apparatus when the wire was heated by the passage of the same current for two seconds.

From observations in an atmosphere of hydrogen, oxygen, nitrogen, and air and in a vacuum, it has been found that the disintegration process is characterised by the emission of two sets of nuclei. The first set, which are got rid of after continuous experimenting, depends on the presence of hydrogen and other gases in the metal. The emission of the second set is conditioned by the presence of oxygen in the neighbourhood of the heated metal, and also on the attainment of a certain definite temperature.

In regard to the first set of nuclei, it has been found that they are emitted at comparatively low temperatures, the minimum temperature at which they can be detected falling as the pressure of the surrounding gas is diminished. The power of emitting these nuclei is temporarily lost when emission has been taking place for some time, but is gradually regained when the metal is allowed to remain unheated. The emissive power is immediately regained when hydrogen is brought into contact with the metal, whereas air, oxygen, and nitrogen do not produce this effect. If, however, the metal has been kept at a white heat in a vacuum for a long time, hydrogen also fails to restore the power of emitting the first type of nuclei. The fact that the nuclei diminish in size and disappear soon after their liberation indicates that these nuclei are not of the nature of solid particles, and it is suggested that they may be either minute drops of water or traces of compound gases produced by the union of hydrogen with other occluded gases.

The second set of nuclei are probably particles of an unstable oxide of the metal, this view being in agreement with the fact that oxygen is necessary for their production, that they begin to be formed at a fairly definite temperature, are very persistent, do not alter in size, and are unaffected by light or by an electric field.

At temperatures where the rate of loss of weight of platinum, rhodium, and iridium is immeasurably small in nitrogen, hydrogen, or a vacuum, the rate is very considerable in oxygen. At a given temperature, the rate of loss for platinum and rhodium is approximately proportional to the oxygen pressure, and in the case of

iridium it increases much more rapidly than the pressure. From experiments with platinum, in which the loss of weight of the metal was compared with the diminution in the quantity of oxygen in the surrounding gas, it was found that in pure oxygen the ratio corresponded approximately with the formation of the oxide PtO_2. In air, the ratio of oxygen absorbed to platinum disintegrated was much smaller, but this would be readily accounted for on the very probable view that the oxide PtO_2 dissociates on cooling. Similar experiments with iridium gave numbers in close agreement with those required for the formation of the oxide IrO_2.

From these facts the author draws the conclusion that the disintegration of platinum, rhodium, and iridium in air at high temperatures is conditioned entirely by the formation of volatile oxides of the formulæ PtO_2, RhO_2, and IrO_2.

Palladium behaves quite differently from the above three metals, and the disintegration in this case appears to be due to simple volatilisation of the metal. The fact that palladium does not yield nuclei of the second type is quite consistent with this view.

The deposits which are obtained on the walls of the vessel containing the electrically heated metals have also been examined, and these observations are consistent with the above views relative to the disintegration process.   H. M. D.

Mineralogical Chemistry.

Asphalt Veins in Quartz-Porphyry near Heidelberg WILHELM SALOMON (*Zeitsch. Kryst. Min.*, 1913, **51**, 634; from *Ber. Oberrhein. Geol. Ver.*, 1909, **42**, 116—123).—A black asphalt with conchoidal fracture occurs with minute quartz crystals in crevices in the porphyry of Dossenheim. Analyses by Ebler gave: C, 77·8—79·8; H, 7·7—8·0; N, 0—2·7; S, 2·2—2·8; ash, 1·0%. Optically active substances being absent, there is no evidence of organic origin; and it is not improbable that the material has been deposited by thermal waters.   L. J. S.

[**Minerals from Sierra Mojada, Coahuila, Mexico.**] FRANK R. VAN HORN (*Amer. J. Sci.*, 1913, [iv], **35**, 23—30). -A description is given of 21 mineral species found in the Veta Rica mine. The ores of silver, lead, and copper occur in a gangue of gypsum and barytes near the contact of Cretaceous limestone with rhyolite. The following analyses, by N. A. Dubois, are given: I, of argentite; II, of proustite :

	Ag.	Cu.	As.	Sb.	S.	Total.	Sp. gr.
I.	86·18	0·70	—	—	13·18	100·06	7·40
II.	64·65	0·70	15·25	trace	0·18	100·78	5·60

            L. J. S.

The Bauxite Question. FRAN TUĆAN (*Centr. Min.,* 1913, 65—68).—A discussion of previous papers (A., 1912, ii, 357; this vol., ii, 64, 69).—Bauxite is a mixture of minerals, and cannot be regarded as a definite aluminium hydroxide. Adsorption combinations of colloidal aluminium hydroxide and hydrated silica cannot always be distinguished by chemical and microscopical means from homogeneous materials.   L. J. S.

Some Minerals from Tuscany. ERNESTO MANASSE (*Jahrb. Min.,* 1912, ii, Ref. 343—346; from *Mem. Soc. Toscana Sci. Nat.,* 1911, **27**, 19 pp.).—Millerite, a species not before recorded from Tuscany, occurs sparingly as fine needles with marcasite in a calcite vein intersecting black clay-slate in the antimony mine of Cetine di Cotoruiano.

Turgite occurs in the Rio Marino mine at Rosseto, Elba, as thin crusts and stalactites on limonite. It is fibrous, steel-grey, and lustrous, and has previously been mistaken for goethite. Analyses I—III (I, fibrous-lamellar; II, fibrous-radiated; III, stalactitic). Formula $H_2Fe_4O_7$.

Goethite is found in an iron mine at Capo d'Arco, Elba, as thin, fibrous crusts on limonite. Analysis IV. Formula $HFeO_2$:

	SiO_2.	Fe_2O_3.	H_2O.	Total.	Sp. gr.
I.	2·65	92·60	5·56	100·81	—
II.	2·11	92·04	5·58	99·73	4·34
III.	1·18	93 54	4·95	99·67	—
IV.	3·21	87·10	10·11	100·42	4·17

Zinciferous rhodochrosite ("ziucorhodocbrosite") as imperfect crystals and rounded masses of a rose-red colour and vitreous lustre on the turgite (see above) from Rosseto, Elba. Analysis V, corresponding with 50% $MnCO_3$, 45% $ZnCO_3$:

	CO_2.	FeO.	MnO.	ZnO.	CaO.	MgO.	Total.	Sp. gr.
V.	36·60	0·66	30·17	31·03	2·10	0·05	100·61	3 86

Jarosite occurs at Capo d'Arco, Elba, as a thin encrustation on, and as small nodules in, limonite. It is brown with an adamantine lustre, and under the microscope the minute, rhombohedral crystals are transparent and gold-yellow. Analysis VI corresponds with 91·17% jarosite, the remainder being admixed quartz and limonite. Jarosite [natrojarosite, A., 1902, ii, 666] occurs also at Capo Calamita, Elba, as a thin encrustation on limonitic ores. Analysis VII corresponds with 95·33% jarosite:

	SiO_2.	SO_3.	Fe_2O_3.	K_2O.	Na_2O.	H_2O.	Total.
VI.	2·16	28·71	48·68	7·82	1·77	[10·36]	100·00
VII.	1·20	31·61	50·28	0·98	5·55	[10·38]	100·00

Alunogen from Vigneria, Elba, is white when pure, but frequently green from admixed melanterite and ihleite; it also encloses small crystals of iron-pyrites. Analysis VIII corresponds with 88·37% of alunogen, $Al_2(SO_4)_3,16H_2O$.

Fibroferrite from Capo Calamita, Elba, is finely fibrous with yellowish-green colour and silky lustre, D 2·08—2·09. Analysis IX ——— ds with $Fe_2O(SO_4)_2,10H_2O$. At 98—100° 23·02% water

is expelled, and at 285° 35·60%, with a gradual change in the optical characters. All the water is re-absorbed from a moist atmosphere, and it is therefore regarded as water of crystallisation. Fibroferrite also occurs at Vigneria and at Capo d'Arco, in Elba:

	SO_3.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	K_2O.	Na_2O.	H_2O.	Insol. in water.	Total.
VIII.	37·80	14·30	0·42	2·16	trace	0·45	0·21	44·31	0·24	99·89
IX.	32·03	—	30·58	1·50	—	—	—	36·40	—	100·51

L. J. S.

The Stassfurt Deposits. MICHAEL RÓZSA (*Zeitsch. Elektrochem.*, 1913, **19**, 109—115).—This paper is divided into two parts, the first of which is theoretical and shows that the nature of the Stassfurt deposits is not in accord with the theory "that the area over which the deposits were formed was separated from the ocean by a bar,'" but rather that irregular floods took place, and that these with the evaporation periods are capable of explaining the peculiarities of the deposits. The layers of hard salt are held to be the product of changed deposits. The second part of the paper gives a comparative table of the layers found in the Kieserite-Carnallite region and the hard salt region. The relative thicknesses of the various layers are indicated. J. F. S.

Question of the Identity of Podolite and Dahllite. VLADIMIR TSCHIRVINSKI (*Centr. Min.*, 1913, 97—102).—Podolite, described as a new mineral by Tschirvinski (A., 1907, ii, 481), has been suggested by Schaller (A., 1910, ii, 1076) to be identical with dahllite. The following new analysis of a podolite concretion from the village of Krutoborodinzy, govt. Podolia, Russia, agrees with the formula previously given, with the addition of a little water, namely, $3Ca_3(PO_4)_2,CaCO_3,\frac{3}{4}H_2O$:

CaO.	P_2O_5.	CO_2.	F.	SiO_2.	Organic matter.	Water of crystal-lisation.	Hygro-scopic water.	Undetermined (Al_2O_3, Fe_2O_3, alkalis, etc.)
50·72	37·08	4·32	0·29	4·18	0·52	1·16	0·37	[1·36]

Analyses of dahllite, on the other hand, lead to the formula $2Ca_3(PO_4)_2,CaCO_3,nH_2O$, where $n=\frac{1}{2}-1$. The two minerals are therefore regarded as being chemically distinct. In physical characters they, however, show little difference; but here podolite approaches francolite and staffelite more nearly than dahllite.

L. J. S.

Mineralogy of the [Russian] Phosphorite Deposits. JAKOV SAMOILOV (*Jahrb. Min.*, 1912, ii, Ref. 338—339; from *Arb. Komm. Moskauer Landw. Inst. Erforschung der Phosphorite*, 1911, **3**, 671—690).—The following analysis is of an unweathered phosphatic nodule of Jurassic age from a boring at Moscow, corresponding with $Ca_3(PO_4)_2$ 46·96, CaF_2 3·74, $CaCO_3$ 10·41, $MgCO_3$ 1·71%:

CaO.	MgO.	Al_2O_3.	Fe_2O_3.	Mn_2O_3.	K_2O.	Na_2O.	P_2O_5.	CO_2.	F.
39·08	0·82	1·70	1·67	trace	0·92	0·99	21·51	5·47	1·82

SiO_2.	FeS_2.	Loss on ignition.	Organic matter.	Insoluble.	Total (less O for F).
0·47	2·52	3·91	0·61	19·43	100·16

According to their external appearance, Russian phosphorites are divisible into two classes: (1) Nodules with a dark, lacquer-like surface, either polished or dull. These show an increasing amount of phosphate from the interior to the exterior; for example, a nodule from the village Wopilowka, govt. Pensa, contained in the interior portion: P_2O_5, 23·89, and insoluble material, 18·22%, and in the exterior portion P_2O_5, 26·81, and insoluble, 4·5%. (2) Nodules with a light-coloured, grey, earthy exterior, due to chemical alteration; here in the exterior portion the phosphate is reduced in amount, and the insoluble material increased.   L. J. S.

Occurrence of Scorodite in Rhodesia. A. E. V. ZEALLEY (*South African J. Sci.*, 1911, **8**, 133—134).—Compact or crystallised scorodite occurs together with mispickel, limonite, and quartz in several auriferous districts in Rhodesia. A mixed sample of amorphous and finely crystallised green scorodite from Gwanda gave on analysis by J. B. Bull:

As_2O_5.	Fe_2O_3.	H_2O.	Total.
50·53	33·49	15·98	100·00

L. J. S.

Uranium Minerals from Prov. Itasy, Madagascar. ALFRED LACROIX (*Bull. Soc. franç. Min.*, 1912 [*i.e.*, 1913], **35**, 233—235).— The new species betafite (A , 1912, ii, 567) has been found as fine crystals (octahedron with rhombic dodecahedron) at some other localities in Madagascar. Analysis I, by Pisani, is of betafite, D 3·75, from Ambalahazo. The mineral is readily attacked by acids, giving a yellow solution, the uranium being present as UO_3 (not as UO_2, as previously stated):

Cb_2O_5. Ta_2O_5. TiO_2. SnO_2. ThO_2. UO_3 ($Ce,La,Di)_2O_3$. Al_2O_3. Fe_2O_3. MgO. CaO. PbO. H_2O. Total.
I. 34·50 1·00 16·20 0·27 1·12 27·15   1·00   1·50 0·50 trace 3·12 0·38 12·39 100·00

Euxenite, occurring as crystals in association with betafite and green apatite in pegmatite at Andibakely, gave analysis II, by Pisani:

Cb_2O_5. TiO_2. ThO_2. UO_3. $(Y,Er)_2O_3$. Ce_2O_3. $(La,Di)_2O_3$. Al_2O_3. Fe_2O_3. CaO. H_2O. Total.
II. 35·50 23·60 3·70 3·00 20·80 0·40 1·70 1·31 1·69 4·01 4·35 100·06

L. J. S.

The Chemical Constitution of the Kaolinite Molecule. II. JOSEPH W. MELLOR and A. D. HOLDCROFT (*Trans. Eng. Ceramic Soc.*, 1911-12, **11**, 169—172. Compare A., 1911, ii, 607).—The composition of a specimen of crystalline kaolinite is as follows:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	K_2O.	Na_2O.	Loss on ignition.
45·04	—	38·58	0·14	0·01	0·38	0·18	0·13	15·94

The loss on ignition included: H_2O, 14·44, and C, 0·80%.

The heating curve was determined, and also the loss of water occurring at different temperatures, the results showing that there is no definite temperature of dehydration, even with well-defined crystals.

The kaolinite used was obtained from the coalfield of Glamorganshire, and has been described by Butler (*Min. Mag.*, **16**. No. 73).

T. S. P.

Mineralogy of Renfrewshire. ROBERT S. HOUSTON (*Trans. Paisley Nat. Soc.*, 1912, **1**, 1—88).—A review is given of the literature relating to the seventy-six species of minerals that have been found in Renfrewshire, and several new analyses are given (compare A., 1909, ii, 63). Analysis I is of native copper from Boylestone:

Cu.	Fe.	CuO.	Fe₂O₃.	CaO.	MgO.	Insol.	Total.
95·61	0·56	1·02	0·80	0·58	0·28	1·20	100·06

II, olivine from Gleniffer; III, ferrite from Gleniffer; IV—VI, prehnite from Boylestone; VII—IX, analcite from Boylestone; X, analcite from Bardrain; XI—XII, thomsonite from Boylestone; XIII—XV, saponite from Boylestone; XVI, saponite from Kilbarchan; XVII, saponite from Bridge of Weir; XVIII, saponite (variety bowlingite) from Boylestone. Analyses are also given of impure samples of chalcocite, iron-pyrites, quartz, wad, and chalybite:

	SiO₂.	Al₂O₃.	Fe₂O₃.	FeO.	MnO.	CaO.	MgO.	Na₂O.	H₂O.	Total.	Sp. gr.
II.	43·31	15·46	6·72	5·54	—	17·82	8·87	0·84	1·86	100·42	
III.	15·68	5·40	61·47	—	trace	2·03	10·41	—	5·04	100·03	
IV.	42·02	27·92	trace	—	—	23·82	1·23	-	5·40	100·39	2·858
V.	40·22	24·64	4·22	—	—	25·02	—	1 16	5·20	100·46	2·918
VI.	42·25	27·40	trace	—	- -	25·99	—	—	3·87	99·51	
VII.	54·42	23·02	—	—	—	0·95	0·26	13·36	8·20	100·21	
VIII.	52·83	24·69	trace	—	—	0·33	-	12·92	9·60	99·43	2·168
IX.	54·22	23·42	trace	—	—	0·42	0·38	13·68	8·20	100·32	—
X.	55·31	22·89	—	—	—	0·63	0·13	13·49	8·40	100·85	2·252
XI.	33·86	32·24	—	· ·	—	16·22	trace	3·63	14·20	100·15	—
XII.	41·45	27·71	—	trace	—	13·61	0·51	3·81	12·30	99·89	
XIII.*	33·96	16·14	8·00	8·93	—	7·10	7·49	0·98	13·62	99·89	—
XIV.†	36·65	5·61	4·69	5·33	—	4·01	17·29	2·55	20·44	99 72	2·224
XV.	32·62	17·82	3·70	8·21	0·62	—	21·26	2·41	13·91	100·55	2·426
XVI.	35 02	22·82	4·16	3·55	—	1·22	23·99	0·40	9·14	100·30	—
XVII.	40·43	9·33	1·12	3·74	—	2·06	23·36	2·87	17·10	100·01	2·239
XVIII.‡	29·71	22·01	1·60	15·41	trace	4·19	15·39	—	11·49	99·80	

* Also CO₂ 3·17.   † Also CO₂ 3·15.   ‡ Also CO₂ trace.

L. J. S.

Origin of Moldavites and similar Sporadic Glasses. GEORGE P. MERRILL (*Jahrb. Min.*, 1912, ii, Ref. 351; from *Proc. U.S. Nat. Mus.*, 1911, **40**, 481—486).—A meteoric origin having been ascribed to the so-called tektites (a general term to include moldavites, billitonites, and australites), the author has examined a series of obsidian pebbles from various localities in North and South America and from Iceland. These are of undoubted terrestrial origin, and they show the same peculiarities of surface markings as the typical tektites. The following analysis of an obsidian pebble from Cali, dep. Cauca, Colombia, is compared with published analyses of tektites, from which it does not appreciably differ:

SiO₂.	TiO₂.	Al₂O₃.	Fe₂O₃.	MgO.	CaO.	Na₂O.	K₂O.	H₂O.	SO₃.	Total.
75 87	trace	14·35	0·22	0·29	nil	3·96	4·65	0·33	0·23	99·90

L. J. S.

Chloritoid (Ottrelite) from the Apuan Alps, Tuscany.
ERNESTO MANASSE (*Jahrb. Min.*, 1912, ii, Ref. 329—330; from *Mem. Soc. Toscana Sci. Nat.*, 1910, 26, 23 pp.)—The ottrelite of the ottrelite-schists of the Apuan Alps is proved on optical and chemical grounds to be identical with chloritoid. Those analyses of ottrelite which show an excess of silica may be explained by the presence of admixed quartz. The optical characters are stated in detail, and the following analyses are given of ottrelite from: I, Stazzema; II, Camporaghena, near Fivizzano; III, Corchia. These agree with the chloritoid formula $H_2O,(Fe,Mg)O,(Al,Fe)_2O_3,SiO_2$. The ratios of $Fe_2O_3 : Al_2O_3$ range from 1 : 10·81 to 1 : 23·99, and of $MgO : FeO$ from 1 : 2·85 to 1 : 7·31 :

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	H_2O.	Total.	Sp. gr.
I.	24·37	trace	37·03	5·36	21·91	0·52	0·16	4·32	7·16	100·83	3·44
II.	26·07	trace	37·01	3·97	24·76	trace	0·12	1·90	7·03	100·86	3·51
III.	25·36	trace	38·99	2·54	23·06	trace	0·24	3·16	7·28	100·63	3·58

L. J. S.

Composition of Some Minerals of the Chloritoid Group.
ERNESTO MANASSE (*Jahrb. Min.*, 1912, ii, Ref. 330—333; from *Proc.-verb. Soc. Toscana Sci. Nat.*, 1911, 20, 29—42).—Previous analyses are quoted and discussed; the variations shown by them may be explained by the impurity of the materials analysed. The following new analyses are given of carefully selected material: I, Masonite from Natick, Rhode Island. II, Sismondine from Champ de Praz, Aosta, Piedmont. These two analyses agree closely with the formula $H_2R''R'''_2SiO_7$. Associated with the sismondine is a chloritic mineral, which gave analysis III, corresponding with $H_{20}Mg_{10}Fe_2Al_6Si_7O_{45}$. IV, Ottrelite from Ottrez, Ardennes. Under the microscope this material is seen to contain a considerable amount of quartz, together with small quantities of magnetite and ilmenite. Deducting 24·38% of admixed quartz, the formula agrees with that given above; corrected D 3·44. V, Ottrelite from a quartz-phyllite on Mt. Fenouillet, near Hyères (Var), contains an excess of 7·65% silica as admixed quartz; corrected D 3·68. VI, Venasquite from Vénasque, Pyrenees, contains 17·98% admixed quartz; corrected D 3·56 :

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	H_2O.	Total.	Sp. gr.
I.	24·56	34·57	5·93	27·20	1·14	—	0·36	6·64	100·40	3·54
II	25·36	42·58	0·72	18·02	0·53	0·18	5·96	7·50	100·85	3·45
III.*	28·06	21·25	—	9·75	—	—	27·46	11·78	99·15	—
IV.	42·93	29·60	0·86	15·43	3·75	—	2·12	5·48	100·17	3·25
V.†	29·71	34·35	4·71	20·33	1·41	1·16	1·69	6·64	100·00	3·60
VI.	37·87	31·12	3·25	20·48	0·62	trace	1·44	5·80	100·58	3·40

* Also Na_2O, 0·55; K_2O, 0·30. † Also TiO_2, trace.

L. J. S.

Minerals from Ambatofotsikely, Madagascar. ALFRED LACROIX (*Bull. Soc. franç. Min.*, 1912 [*i.e.* 1913], 35, 231—233).—The pegmatites at this locality, situated 27 km. west of Miandrarivo, contain abundance of ampangabeite (A., 1912, ii, 567), fine crystals

of monazite (A., 1913, ii, 69), and fragments of orthite. This orthite, D 3·48, is rich in thoria; the following analysis by Pisani corresponds with the formula

$$[(Si,Th)O_4]_{11}(Al,Ce,La,Di,Fe)_8(Ca,Fe,H_2)_{10}:$$

SiO_2.	ThO_2.	Al_2O_3.	Ce_2O_3.	$(La,Di)_2O_3$.	$(Y,Er)_2O_3$.	Fe_2O_3.	FeO.	MnO.	CaO.	H_2O.	Total.
32·00	5·60	12·40	9·08	7·38	0·40	4·50	11·60	0·54	15·68	1·24	100·84

<div align="right">L. J. S.</div>

Lavas from Central Madagascar. ALFRED LACROIX (*Compt. rend.*, 1913, **156**, 175—180).—Twenty-seven detailed analyses, by Boiteau, are given of rocks from the volcanic districts of Ankaratra and Itasy. They range from rhyolite, with 71·45% silica, to nephelinite, with 38·74% silica. <div align="right">L. J. S.</div>

Ilmenite from the Quarries of Potstone at Sasso di Chiesa (Val Malenco). L. MAGISTRETTI (*Atti R. Accad. Lincei*, 1912, [v] **21**, ii, 761–767).— A crystallographic study of this mineral, which has D 4·55, and the following composition:

[With A. MORESCHI]:

SiO_2.	TiO_2.	Fe_2O_3.	FeO.	MnO.	Al_2O_3.	MgO.	Total.
0·65	47·20	33·50	15·00	1·34	1·00	0·90	99·59

<div align="right">R. V. S.</div>

Meteorite of Gumoschnik, Bulgaria. G. BONTSCHEW (*Jahrb. Min.*, 1912, ii, Ref. 354—355; from *Periodičesko spisanie, Sofia*, 1910, **71**, 373—390).—A meteoric fall was observed on April 28th, 1904, near the village of Gumoschnik, in the Trojan district. Five or six stones, with a total weight of 5669 grams (the largest 3815 grams), were picked up. The material consists of olivine, enstatite, augite, iron, pyrrhotite, chromite, and a fine-grained to compact mass of undetermined nature. Chondrules of olivine and enstatite are set in a brecciated groundmass. The following analyses are of: I, the magnetic portion; II, the non-magnetic portion; and III, the bulk analysis. The amount of nickel is unusually low:

	Fe.	Ni.	Fe_7S_8.	SiO_2.	Cr_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	Lost on ign.	Total.
I.	87·141	2·435	2·028			28·310						99·914
II.	—	—	—	45·989	0·002	22·834	4·682	0·130	2·460	23·470	—	100·978
III.	15·012	0·467	0·493	42·363	0·048	15·872	3·286	0·147	1·216	18·808	0·364	100·734

<div align="right">L. J. S.</div>

Existence of Natural Ozonised Waters and Probable Theories of the Phenomenon. The "Acqua Forte" of the Bagnore of Monte Amiata. RAFFAELE NASINI and C. PORLEZZA (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 740—750, 803—811; *Chem. Zeit.*, 1913, **37**, 129.—The authors have discovered two natural waters which contain ozone as a normal constituent, and in such quantity as to smell plainly of the gas. The acid waters of the Bagnore of Monte Amiata are highly ozonised, and those of the springs of the Bagnoli in the same region in smaller degree. The

data in the present paper refer to the former water. In one litre of it at 21·5°, the following gases are dissolved: carbon dioxide, 543·72 c.c.; oxygen, 1·26 c.c.; ozone, 0·135 c.c.; the inert gases were not determined. The gases arising from the water at the source have the following composition (per 100 c.c.): carbon dioxide, 93·45 c.c.; oxygen and ozone, 0·15 c.c.; residue unabsorbed, 6·40 c.c.; the ozone amounted to 0·00064 c.c. Dispersion experiments showed that the air above the well contained 1838 ions per c.c., whilst the number in the ordinary air of the locality did not exceed 1000 per c.c. From experiments with water in which known amounts of ozone had been dissolved, it was found that the odour is still perceptible when 0·037 c.c. of ozone is dissolved in one litre of water, and the limit of sensibility of the iodide starch reaction is not reached at 0·02 c.c. per litre. For this and other reasons the authors are sceptical concerning the few other alleged ozonised waters mentioned in the literature. As possible explanations, the authors suggest the autoxidation of ferrous salts, either alone or in conjunction with ferruginous micro-organisms. The water contains 0·001565 gram of iron per litre, probably in the form of ferrous hydrogen carbonate, which is known to be an autoxidisable substance. Attention is drawn to the possible therapeutic value of the waters.   R. V. S.

Analytical Chemistry.

Hempel Double Pipette Modified to Facilitate Filling. ALEXANDER CHARLES CUMMING (*J. Soc. Chem. Ind.*, 1913, **32**, 9).—A side-tube, opening vertically, is fitted to the second bulb from the burette, and this enables the pipette to be filled as easily as a simple pipette. The pipette is first filled with an indifferent gas by passing it through, whilst the additional side-tube is closed with a cork. The reagent is then introduced through the side-tube, and water is poured into the two last bulbs, through the exit-tube from the last bulb, to form a water seal. The side-tube is then closed with a well-fitting rubber cork.   T. S. P.

Micro-chemical Reagents. WILHELM LENZ (*Zeitsch. anal. Chem.*, 1913, **52**, 90—99).—Directions are given for preparing absolutely pure reagents (acids, ammonia, alcohol, platinum chloride, ammonium uranyl acetate, ammonium cobalt thiocyanate, metallic tin and zinc) for use in micro-chemical testing.

Glass utensils and slides should not be used. The reagents should be kept in flasks made of fused silica; the distilled water should be stored in a, preferably gilded, silver flask.   L. DE K.

Apparatus for Electrolytic Estimations. FELIX CHANCEL (*Bull. Soc. chim.*, 1913, [iv], **13**, 74—76).—The bottom of a test-tube, 30 × 125 mm., made of thin Jena glass, is pierced by a

platinum-iridium wire 1 mm. in diameter and 50 mm. long, of which 40 mm. are inside the tube and 10 mm. outside. This serves as an anode, and is connected by a clip with a silver or copper wire bent twice at right angles, and then brought parallel to the length of the tube and secured to the upper portion of the latter, where, when the apparatus is in use, it is connected to the positive pole of the battery. The cathode consists of a cylinder of platinum gauze, 20×30 mm., hung inside the tube by a platinum wire 110 to 120 mm. long, which is attached to a support in the usual way. In use the tube is closed by a watch glass suitably pierced to take the suspending wire. T. A. H.

The Use of an Extract of Red Cabbage as an Indicator for the Measurement of the Hydrogen Ion Concentration. L. E. WALBUM (*Biochem. Zeitsch.*, 1913, 48, 291—296).—The alcoholic extract of red cabbage can be used as an indicator for concentrations between $p_H = 2.0$ and $p_H = 4.5$, within which limits results agreeing closely with those by the electrometric method can be obtained. Good results are obtained even in the presence of relatively large amounts of proteins, which are not affected by the presence of salts (even $\frac{1}{2}M$-sodium chloride), toluene, or chloroform. S. B. S.

Estimation of Moisture. GEORGE N. HUNTLY and JOHN H. COSTE (*J. Soc. Chem. Ind.*, 1913, 32, 62—67).—In considering the question of the estimation of moisture in commercial products, the authors mention in some detail the various methods which are employed for the purpose. These methods are divided into three groups, namely: *Direct methods*. 1. Water driven off by ignition, condensed in part of the ignition tube and weighed directly. 2. Substance heated in a current of dry gas, or in a vacuum, water vapour collected in calcium chloride or sulphuric acid, and weighed. 3. Substance mixed with an excess of a volatile, non-miscible liquid, such as xylene, distilled, and the water measured under the hydrocarbon layer. 4. The substance is heated directly to 130° by a vapour (high pressure steam) jacket, the steam given off condensed, and measured. *Gasometric methods*. 5. The substance is mixed with calcium carbide; acetylene measured. 6. The substance is mixed with magnesium methyl haloid in the presence of a suitable dry solvent; methane measured. 7. The substance is treated with sodium; hydrogen measured. *Indirect methods*. 8. Estimation of the loss of weight by heating to a definite or indefinite temperature (the usual method). 9. Prolonged exposure in a vacuum in the presence of sulphuric acid, either at ordinary or at a higher temperature. Most of the methods are trustworthy under particular conditions and when they are applied to suitable substances. Special attention is given to the last two methods mentioned, and it is recommended that care should be taken to have the temperature inside the ordinary drying oven as nearly as possible 100°; for general work a few degrees higher will be found to be more satisfactory. In the method where the substance is dried in a vacuum,

the pressure should be as low as possible; and the exposed surface of the sulphuric acid large. When applied to coals, this method yields results which are invariably higher than those obtained by drying the coal in a water-oven.   W. P. S.

Estimation of Moisture in Organic Substances. F. H. CAMPBELL (*J. Soc. Chem. Ind.*, 1913, **32**, 67—70).—The calcium carbide method is recommended for the estimation of moisture in such substances as coal, coffee, cocoa, tea, butter, etc.; in the process employed by the author, the amount of acetylene evolved is estimated gravimetrically, and an apparatus is described for this purpose. The results obtained agree closely with those found by drying the substances under reduced pressure over sulphuric acid.
                                                                W. P. S.

Estimation of Moisture in Foods and Other Organic Substances. WILLIAM P. SKERTCHLY (*J. Soc. Chem. Ind.*, 1913, **32**, 70).—Results are recorded which show that many organic substances yield more moisture when dried under reduced pressure in the presence of sulphuric acid than when they are heated to constant weight in the ordinary steam-oven. The difference was most marked in the case of farinaceous substances, amounting in one instance (arrowroot starch) to 2%. It was also found that flours, meals, etc., increased in weight when heated for more than two hours at 100°.   W. P. S.

Colour Reaction of Chlorates. JOSEPH PIERAERTS (*Bull. Soc. chim.*, 1913, [iv], **13**, 104—109; *Bull. Assoc. chim. Sucr. Dist.*, 1913, **30**, 401—406).—When 1 c.c. of a 0·5% potassium chlorate solution is treated with 5 c.c. of a 2·5% aqueous aniline solution and 6 c.c. of concentrated hydrochloric acid, a red coloration is obtained which changes in a few minutes to blue. The test is not to be trusted when the potassium chlorate solution contains less than 0·1% of the salt, but 0·05% solutions yield a coloration when the aniline solution is prepared with 50% alcohol. The blue coloration may be extracted from the mixture by shaking with chloroform, ether, or amyl alcohol. The test is useless in the presence of iodates, as these yield a similar coloration to that obtained with chlorates. W. P. S.

Disturbing Influence of Alcohol on Various Reactions. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1913, **83**, 164—165)— When half a volume of alcohol is added to a potassium iodide solution to which chloroform, a few drops of sulphuric acid, and a solution of nitrite are also added, instead of the characteristic violet colour being formed in the chloroform layer after shaking, an orange or reddish-yellow coloration is obtained. Methyl or amyl alcohol, ethyl acetate, and acetone have a similar disturbing influence.

The characteristic colour reaction of phenol with ferric chloride is also entirely altered by the presence of alcohol, a dirty green or yellow coloration being obtained instead of the characteristic blue.
                                                                E. F. A.

Estimation of Hydriodic Acid in Tincture of Iodine.
ANDRÉ LECLÈRE *(J. Pharm. Chim., 1913, [vii], 7, 68—69).—In
general, iodine is estimated in tincture of iodine by titration with
sodium thiosulphate, and then the hydriodic acid is determined by
adding potassium iodate solution and titrating the iodine set free.
It is pointed out that this last estimation is subject to two sources
of error. If the iodate solution used is not exactly neutral, an
excess of iodine is liberated. Further, the amount of hydriodic acid
is frequently calculated from the equation $HIO_3 + 5HI = 6I + 3H_2O$
instead of from the relation $KIO_3 + 6HI = KI + 3H_2O + 6I$, which
correctly represents what takes place. T. A. H.

A New and Delicate Test for Oxygen. KARL BINDER and
RUDOLF F. WEINLAND (Ber., 1913, 46, 255—259).—The authors have
previously shown that the deep red solutions formed when ferric
salts and catechol are mixed in alkaline solution contain the salts
of an acid $H_3[Fe(C_6H_4O_2)_3]$ (compare A., 1912, i, 184, 445). They
have now found that if ferrous sulphate is used instead of ferric
salts, no colour is produced, but that oxygen is very rapidly
absorbed from the air, giving the red colour. The formation of this
red colour is an exceedingly delicate test for oxygen, and the
authors have devised a special apparatus in which the respective
solutions can be prepared and mixed in an atmosphere of oxygen-
free hydrogen and then brought into contact with the gas which
is to be tested for oxygen. The authors were able to detect oxygen
in the Tübingen coal gas, and in carbon dioxide used in the esti-
mation of nitrogen by Dumas's method.

The alkaline solution of ferrous sulphate and catechol can be
used in the Hempel pipette for the absorption of oxygen in gas
analysis. For quantitative absorption, it is necessary to shake
vigorously for five minutes. T. S. P.

**Estimation of Available Oxygen in Persalts and Washing
Powders with Titanium Trichloride.** LUDWIG MOSER and F.
SEELING (Zeitsch. anal. Chem., 1913, 52, 70—85).—Perborates may be
titrated by dissolving about 0·25 gram of the salt (or about 3 grams
of washing powder) in water, 25 c.c. of dilute sulphuric acid are
added, and while passing a current of carbon dioxide the liquid is
titrated with standard titanium trichloride, the end point being
shown by the disappearance of the yellow pertitanic colour. Two
mols. of titanium trichloride = 1 mol. of sodium perborate. In the
case of washing powders it is advisable to add, before titration, some
carbon tetrachloride to dissolve the separated fatty matter; or a
definite volume of titanium trichloride may be added, and the
excess titrated as usual by means of ferric chloride.

Percarbonates may be tested similarly, but as the direct titration
is attended with loss of oxygen, the solution should be delivered
from a pipette which dips into a known volume of titanium tri-
chloride in an atmosphere of carbon dioxide. The excess of titanium
is then titrated with ferric chloride. Two mols. of titanium tri-
chloride = 1 mol. of potassium percarbonate. Persulphates are
treated like percarbonates. L. DE K.

Apparatus for the Estimation of Sulphur in Steel and **Iron.** GEORG PREUSS (*Chem. Zeit.*, 1913, **37**, 82).—After the material
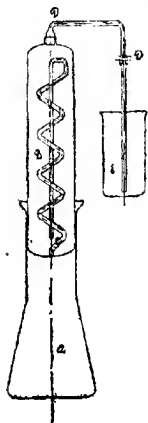
to be tested has been placed in the flask *A*, the cooler *B* is filled half way with cold water; this serves for the purpose of cooling and also for the absorption of hydrogen chloride. The cooler *B* is closed with the bent tube *D*. Immediately after introducing the acid, the cooler *B* is placed on the flask *A* in such a manner that the tube *D* dips into the beaker *E*, containing 40 c.c. of cadmium solution. An escape of hydrogen sulphide during this momentary opening is not to be feared. On warming with a small flame, the gases evolved pass through the serpentine tube *C*, penetrate the water column in cooler *B*, and then pass through the beaker *E*, where every trace of hydrogen sulphide is absorbed. The sulphur may then be estimated either gravimetrically or volumetrically.

L. DE K.

A Source of Error in the Kjeldahl-Gunning Process. EM. CARPIAUX (*Bull. Soc. Chim. Belg.*, 1913, **27**, 13—14).—The Gunning modification of Kjeldahl's process (heating with addition of potassium sulphate) does not work well in the case of several vegetable products (alkaloids, for instance). The relation between potassium sulphate and free sulphuric acid towards the end of the operation is also a matter of importance, because a loss of ammonia is to be feared when an insufficiency of free acid is present.

When working as follows these sources of error disappear: 1·5 grams of the sample (sesame cake, for instance) are heated with 30 c.c. of sulphuric acid, and after a while 15 grams of potassium sulphate are added. To make sure of the complete conversion of the nitrogen into ammonia, 1 gram of mercury and 1 gram of dry copper sulphate should also be added. The heating should not be continued longer than necessary, so as to prevent undue loss of acid.   L. DE K.

Estimation of Ammoniacal Nitrogen by means of Formaldehyde. GAILLOT (*Ann. Chim. anal.*, 1913, **18**, 15—17).—When an ammonium salt is treated with formaldehyde, the ammonia combines with the aldehyde to form hexamethylenetetramine, and the acid radicle of the salt is set free; the amount of this free acid, as estimated by titration, is a measure of the ammonia present. For the estimation, a weighed quantity of the ammonium salt is dissolved in water, the solution neutralised, an excess of neutral formaldehyde added, and the resulting acidity of the mixture is titrated, phenolphthalein being used as indicator.   *W. P. S.

Estimation of Nitric Acid by Schloesing's Method. MAURICE CANET (*Bull. Soc. chim. Belg.*, 1913, **27**, 10—11).—This

process, based on the liberation of nitric oxide when a nitrate is boiled with hydrochloric acid and ferrous chloride, does not always give a pure gas, since the author finds that, when treated with pure oxygen and then with alkaline pyrogallol, it leaves an appreciable volume of unabsorbed gas.

One of the sources of error must no doubt be attributed to the use of an indiarubber cork on the distilling flask, which at a high temperature does not completely prevent the entrance of atmospheric air. The error is somewhat counterbalanced, but not removed, when making a check experiment with a known amount of nitrate. If in the testing of nitrocellulose, this is dissolved first in sulphuric acid, the nitric oxide is contaminated with traces of carbon monoxide.   L. DE K.

The Reaction between Formaldehyde and Nitrous Acid.
LUDWIG VANINO and A. SCHINNER (*Zeitsch. anal. Chem.*, 1913, **52**, 21—28).—About 0·25 gram of sodium nitrite is dissolved in water, and boiled in a suitable apparatus until the air has been completely expelled. A sufficiency of formaldehyde is then introduced, followed by hydrochloric acid, when carbon dioxide and nitrogen are evolved. The former is absorbed by aqueous potassium hydroxide, and the latter is then measured with the usual precautions. One atom of nitrogen = 1 mol. of nitrous acid. L. DE K.

Estimation of Nitric Oxide. KOEHLER and M. MARQUEYROL (*Bull. Soc. chim.*, 1913, [IV], **13**, 69—72).—The method described by Baudisch and Klinger (this vol., ii, 74) is not applicable to mixtures containing, in addition to nitric oxide, nitrous oxide, nitrogen, carbon dioxide, and carbon monoxide. In such cases the authors absorb the nitrogen trioxide formed by means of ethylaniline. In the residue, carbon dioxide is estimated by means of potassium hydroxide and the excess of oxygen added is absorbed by alkaline pyrogallol; the rest of the analysis is carried out in the ordinary way. Ethylaniline dissolves a little more than its own volume of carbon dioxide at 15° to 20° under atmospheric pressure, so that when only one-sixth or one-seventh of the total pressure is due to this gas, the volume dissolved by the small amount of ethylaniline used is negligible.   T. A. H.

Estimation of Phosphoric Acid Soluble in Citric Acid in Thomas Slag. W. SIMMERNACHER (*Chem. Zeit.*, 1913, **37**, 145—146. Compare A., 1907, ii, 577; 1912, ii, 992, 993).—When ferric chloride is added to the citric acid solution of the phosphoric acid in order to prevent precipitation of silica, the subsequent addition of the mixture of ammonium citrate solution and magoesia mixture must be made in small quantities at a time, otherwise ferric hydroxide is precipitated and does not re-dissolve in the reagent. •Ferrous chloride does not prevent the precipitation of the silica. The mixture of ammonium citrate solution and magnesia mixture must be freshly made.   W. P. S.

Some Factors Influencing the Quantitative Estimation of **Arsenic in Soils.** J. E. GREAVES (*J. Amer. Chem. Soc.*, 1913, **35**, 150—156).—The methods which have hitherto been recommended for the estimation of arsenic in soils are liable to give inaccurate results, as they do not take into account the effect produced by the presence of iron. A study has now been made of the influence of iron on the estimation of arsenic by Marsh's method and of the effect of stannous chloride in overcoming the retention of arsenic by iron.

The following method has been found to give the best results. To 10 grams of the soil are added 25 c.c. of concentrated nitric acid, and the mixture is heated for thirty minutes. While still fairly hot, 10 c.c. of concentrated sulphuric acid are added, and the mixture is again heated for thirty minutes. The mixture is then filtered, and the soil washed with hot water; the filtrate is evaporated to dryness and heated until free from nitrates. The residue is treated with dilute sulphuric acid and 20 c.c. of 10% solution of stannous chloride, and then slowly introduced into the Marsh apparatus. This method enables very small quantities of arsenic to be estimated accurately.   E. G.

Estimation of Arsenic in Urine and Blood. FRANZ LEHMANN (*Arch. Pharm.*, 1913, **251**, 1—4).—A method described previously in detail by the author and E. Rupp (A., 1912, ii, 866) may be used for the estimation of arsenic in urine and in blood. In the case of urine, 500 c.c. of the sample are treated with 2·5 grams of powdered potassium permanganate and evaporated almost to dryness, a small quantity of solid paraffin being added to prevent frothing. This preliminary treatment with permanganate is essential in order to avoid loss of traces of arsenic during the evaporation. The estimation is then proceeded with as described. Blood (50 grams) is shaken for ten minutes with 2·5 grams of permanganate before the sulphuric acid and the main quantity of permanganate are added.   W. P. S.

The Separation of Arsenic and Tungsten. SIEGFRIED HILPERT and THEODOR DIECKMANN (*Ber.*, 1913, **46**, 152—155).— Owing to the formation of very stable complexes between arsenic and tungstic acids, precipitation methods do not give a satisfactory separation. The authors make use of the distillation method for separating the arsenic, using cuprous chloride as the reducing agent. To the mixture containing the complex of arsenic and tungsten (0·0646 gram of arsenic and 0·1313 to 0·2626 gram of tungstic acid), 15 grams of cuprous chloride are added and 150 c.c. of hydrochloric acid (D = 1·16), and the distillation carried out until only a small residue is left. The distillation is again repeated with another 150 c.c. of hydrochloric acid, after which no more arsenic will pass over. It is found, however, that arsenic still remains in the residue, although there is no definite molecular ratio between the arsenic and the tungsten. It is probable that it is adsorbed by the tungstic acid, since if the residue is made alkaline with potassium hydroxide,

heated, cooled, and then again distilled twice with 150 c.c. of hydrochloric acid, the remainder of the arsenic distils over, and a quantitative separation is attained. The arsenic in the distillate is determined by titration with iodine.

The quantity of tungstic acid should not exceed the amount given above. T.S.P.

Estimation of Carbon and Carbon Dioxide. ACH. GRÉGOIRE, JAMES HENDRICK, EM. CARPIAUX, and E. GERMAIN (*Ann. Chim. anal.*, 1913, **18**, 1—8).—In the method proposed, the substance containing carbon is ignited in a current of oxygen, and the carbon dioxide (after the gases have been passed over copper oxide) is absorbed in barium hydroxide solution. The latter is contained in a Pettenkofer absorption tube, and the resulting barium carbonate is then collected on a filter, precautions being taken to prevent absorption of carbon dioxide from the atmosphere during the filtration. The barium carbonate is next decomposed in a modified Scheibler's apparatus, and the volume of the liberated carbon dioxide is measured. Particular attention is paid to the volume of carbon dioxide which dissolves in the nitric acid employed for the decomposition, and a table is given showing the corrections to be applied on this account. For instance, 10 c.c. of nitric acid, D 1·20 at 16°, absorb 10·67 c.c. of carbon dioxide (calculated to normal temperature and pressure). W.P.S.

Portable Pettersson-Palmqvist Apparatus. R. P. ANDERSON (*J. Amer. Chem. Soc.*, 1913, **35**, 162—168).—A modification of the Pettersson-Palmqvist apparatus for estimating carbon dioxide in air is described, which has the advantages of being more readily and conveniently manipulated than the original form, and of being more easily portable. By means of a coil of copper tubing submerged in the water in the glass cell, the sample of air can be rapidly adjusted to the temperature of the apparatus. Carbon dioxide can be quickly and accurately estimated when present in quantities not exceeding 0·5% by volume. E.G.

The Use of Phenolphthalein and of Roeolic Acid for the Estimation of Free Carbonic Acid in Water. HERMANN NOLL (*Zeitsch. angew. Chem.*, 1913, **26**, 85—87).—Chiefly a reply to Tillmaus and Heublein (A., 1912, ii, 685). Further experiments made by the author indicate that in the titration of the free carbonic acid in water, the hydrogen carbonates behave differently towards phenolphthalein from what they do towards rosolic acid. With the latter indicator, a definite portion of the free carbonic acid is not accounted for, which portion is always proportional to the hydrogen carbonates present. Thus, using a rosolic acid solution of the strength 1:1000, 1 mg. of carbonic acid present as hydrogen carbonate masks the presence of 0·25 mg. of free carbonic acid, whereas with a strength of 1:1500, 0·15 mg. is masked. These results verify those of Tillmans and Heublein with respect to rosolic acid. T.S.P.

Microchemical Reaction for Carbonates in Rock Sections.
W. HEEGER (*Centr. Min.*, 1913, 44—51).—The reagent used consists of
2—3 c.c. $N/10$-hydrochloric acid, to which a few drops of potassium
ferricyanide solution have been added. From the velocity of the
reaction and the intensity of the blue coloration produced, con-
clusions can be drawn as to the presence of various carbonates—
calcite, dolomite, ankerite, etc. Only in very exceptional cases is
calcite so free from iron that no colour is obtained. This method
has the advantage over other colouring methods in being applicable
when the rock constituents are in a finely divided state.   L. J. S.

Qualitative Organic Analysis by means of Magnesium.
JOSÉ GIRAL PEREIRA (*Anal. Fis. Quim.*, 1913, 11, 68—73).—When
organic compounds are ignited with magnesium or, better, with
magnalium, carbon may be detected in the residue by treatment
with ammoniacal cuprous chloride and acidification, nitrogen by
the generation of ammonia on warming with water, and oxygen
by means of the feeble alkalinity of the magnesium oxide. The
oxygen test is not trustworthy, and magnalium gives better results
than magnesium.   G. D. L.

Detection of Silicic Acid in Urine without Incineration.
ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1913, 83, 143—152).—The
urine is partly evaporated and precipitated with alcohol. The
sticky precipitate is stirred with alcohol, brought on to a filter,
washed with alcohol, and dried after washing with ether. It is
then shaken out of the filter, stirred with dilute hydrochloric acid,
and finally returned to the filter, and the insoluble portion well
washed. On incineration, almost pure silicic acid is obtained.
The daily urine contains on the average about 0.1 gram SiO_2.
     E. F. A.

Decomposition of Silicates. WALTHER HEMPEL (*Zeitsch. anal.
Chem.*, 1913, 52, 86—90).—If an electric oven is at disposal by
means of which a temperature of $1360°$ can be obtained, the best
way for rendering silicates soluble is to heat 1 gram of the powdered
sample with 3 grams of pure barium carbonate for ten minutes.
The chief advantage of the process lies in the fact that the barium
is readily removed from the resulting solution by means of sulphuric
acid; also, the platinum crucible does not suffer.   L. DE K.

**General Method for the Analysis of the Ashes of Body
Fluids.** W. MESTREZAT (*J. Pharm. Chim.*, 1913, [vii], 7, 60—65).—
A general method is described for the determinations successively
of phosphoric acid, iron, aluminium, lime, and magnesia on the
same specimen of ash prepared from a body fluid. Estimations of
sodium and potassium are best made on a second specimen of the
ash. The method is particularly applicable to ash from the cerebro-
spinal fluid.   T. A. H.

Evaulation of Barium Sulphide. JULIUS F. SACHER (*Zeitsch.
anal. Chem.*, 1913, 52, 28—31).—To the solution of the sulphide is

added a definite number of c.c. of a solution of lead nitrate (16 grams per litre), a little acetic acid is added, and the lead sulphide is filtered off and washed with cold water. The excess of lead is then titrated with ammonium molybdate (8·526 grams per litre; 1 c.c.=1 c.c. of the lead solution), using a 0·5% solution of tannin as external indicator, 1 c.c. of lead solution=0·0081814 gram of barium sulphide. L. DE K.

Estimation of Magnesium Chloride in Water. EMIL BOSSHARD and W. BURAWZOW (*Zeitsch. angew. Chem.*, 1913, **26**, 70—72). —A known volume of the sample is evaporated on the water-bath, and the residue extracted with a mixture of equal volumes of absolute alcohol and ether, which dissolves any magnesium (and calcium) chloride present. The filtrate is then diluted with water to a definite volume, and in an aliquot part of this the chlorine is estimated volumetrically. In another part, the calcium is estimated gravimetrically, and after allowing for this, the remaining chlorine is calculated to magnesium chloride. L. DE K.

Behaviour of Uric Acid towards Ammonia and Magnesium Salts and the Estimation of Magnesium in Urine. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1913, **83**, 152—159).—When urine is precipitated by magnesia mixture and the precipitate filtered immediately, there is no separation of uric acid. When the filtrate is left for a day or more, in addition to a little ammonium magnesium phosphate, there is a characteristic yellow separation. This substance contains uric acid, ammonia, and magnesia, and represents perhaps a compound of the structure

$$Mg(NH_4)_2(C_5H_2O_3N_4)_2.$$
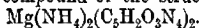
Various unsuccessful attempts to synthesise such a compound are described.

The influence of these observations on the direct estimation of magnesium in urine without incinerating is investigated and proved to be without moment. E. F. A.

Rapid Estimation of Zinc. KURT VOIGT (*Zeitsch. angew. Chem.*, 1913, **26**, 47—48. Compare Abstr., 1912, ii, 298).—The author again proves by a number of experiments that in the presence of sufficient ammonium chloride no insoluble zinc silicate is regenerated on adding ammonia. L. DE K.

Influence of Lead on the Titration of Zinc with Ferrocyanide. VICTOR LENHER and C. C. MELOCHE (*J. Amer. Chem. Soc.*, 1913, **35**, 134—138).—The most satisfactory volumetric method for estimating zinc in ores is the modified Waring method. Conflicting statements have been made with reference to the influence of lead on the titration with ferrocyanide, and this question has therefore been investigated.

The results show that when the titration is carried out in the usual way, the presence of lead is immaterial. In estimating lead by the ferrocyanide method, an acetic acid solution should be used, and mineral acids must not be present.

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In the estimation of zinc in ores in which lead and iron are the only heavy metals present in any considerable quantity, such as the Wisconsin zinc ores, the lead need not be·removed before carrying out the ferrocyanide titration. The ore (0·5 gram) is dissolved in 10 c.c. of concentrated hydrochloric acid and a little nitric acid. After dilution, the solution is treated with ammonia and afterwards filtered. The precipitate is dissolved in dilute hydrochloric acid and reprecipitated with ammonia. The filtrate is added to that from the earlier precipitation, is acidified with hydrochloric acid, and, after being concentrated by evaporation, is ready to be titrated. The solution should be hot when titrated, should have a volume of 200 c.c., and should contain 6—10 c.c. of concentrated hydrochloric acid and 10 grams of ammonium chloride. The ferrocyanide solution should be of such strength that 1 c.c. is equivalent to 0·005 gram of zinc. Solution of uranium nitrate (5%) is the best indicator.   E. G.

Colorimetric Determination of Traces of Zinc. ANGEL DEL CAMPO CERDAN and JOSÉ DE LA PUENTE (*Anal. Fis. Quim.*, 1913, 11, 98—108).—The formation of a blue colour on the addition of aqueous ammonia and resorcinol to zinc solutions may be made the basis of a colorimetric method for the recognition of zinc down to 1^{-7} gram. For every 100 c.c. of liquid, 2 c.c. of 0·92 ammonia and 2 c.c. of 5% resorcinol are added. The liquid is covered with paraffin to exclude oxygen, and after twenty-four hours examined in the colorimeter. The maximum error observed was 6·6%.   G.D.L.

Detection and Colorimetric Estimation of Lead, Copper, and Zinc in Potable Water. LUDWIG W. WINKLER (*Zeitsch. angew. Chem.*, 1913, 36, 38—44).—In the usual colorimetric estimation of lead it is necessary to add to the sample and to the comparison fluid a certain amount of ammonium chloride, otherwise the result will be deceptive.

It is pointed out that in the presence of even traces of suspended ferric hydroxide, the lead will pass into the deposit, so that the water may appear lead-free. Instead of hydrogen sulphide water, the author prefers a solution of sodium monosulphide; both acetic acid or ammoniacal liquids may be used. If copper is also present, the following process is recommended. The copper is estimated colorimetrically by means of ferrocyanide in the presence of potassium hydrogen carbonate, potassium cyanide is added (which causes a green coloration), then an ammoniacal solution of ammonium chloride, and finally sodium sulphide, which will react with the lead only.

A new process is given for the estimation of zinc. The oxide obtained by the usual process is converted by way of a check into chloride, and the chlorine is then titrated with silver in the usual manner after adding a little potassium hydrogen carbonate. Minute traces of zinc are judged from the turbidity caused by the reagents.
                                        L. DE K.

Detection of Traces of Copper. WESLEY B. PRITZ, A. GUILLAUDEU, and JAMES R. WITHROW (*J. Amer. Chem. Soc.*, 1913, **35**, 168—173).—In the course of certain work on the electrolytic precipitation of copper, it was desired to ascertain the sensitiveness of the various reagents which are usually employed to determine whether the metal has been removed completely from the solution. It has been found that, if the volume of the electrolyte is 100 c.c., and 1 gram of copper is originally present and other metals are absent, the end-point can be detected by ammonium hydroxide within 0·105%, by ammonium sulphide within 0·015%, and by potassium ferrocyanide within 0·009%.

The following method is recommended for detecting traces of copper in the solution after electrolytic precipitation has been effected. One c.c. of the sample is introduced into a glass tube, 3—5 mm. in internal diameter, 15 cm. long, and with a capacity of nearly 3 c.c. The solution is rendered alkaline with ammonia, acidified with glacial acetic acid, and then treated with two drops of 2% potassium ferrocyanide solution. If more than 1 mg. of copper is present, a pronounced red coloration is produced, but if there is not more than 0·1 mg. of copper in 100 c.c. of the solution, the colour is practically identical with that of a blank experiment made in a similar tube.   E. G.

Estimation of Copper with ·[Sodium Hypophosphite. RICHARD WINDISCH (*Zeitsch. anal. Chem.*, 1913, **52**, 1—13).—The process, previously recommended by Dallimore (A., 1909, ii, 833), is intended more particularly for commercial copper sulphate. One hundred grams of the sample are dissolved in water, 60 c.c. of dilute sulphuric acid (1 : 7) are added, and the whole diluted to one litre; 50 c.c. are then heated to boiling in a deep porcelain dish with addition of 20 c.c. of commercially pure sodium hypophosphite (200 grams per litre). After fifteen minutes' action, the precipitate, consisting of metallic copper, is collected, washed first with hot water, then with alcohol, and finally converted by ignition into oxide.   L. DE K.

Estimation of Copper in Preserved Vegetables by means of the Spectrophotometer. EUGÈNE TASSILLY (*Bull. Soc. chim.*, 1913, [iv], **13**, 72—74).—The method depends on the complete extraction of the copper from the charred vegetables and its conversion into copper ferrocyanide, which is then estimated by means of a spectrophotometer, previously graduated by means of a similar copper ferrocyanide solution of known strength.

From 10 to 15 grams of the product are ignited gently to produce a charred mass retaining the shape of the original. This is extracted at 100° with 2 to 5 c.c. of sulphuric acid, water added, the solution filtered, and the residue washed. The copper in the filtrate and washings is precipitated by sodium hyposulphite and the precipitate washed and carefully ignited as usual. The residue is dissolved in 1 to 1·5 c.c. of sulphuric acid, a few drops of nitric acid added, and the excess of acid evaporated. The cupric sulphate

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is dissolved in water, 2 c.c. of potassium ferrocyanide solution (0·07 gram per c.c.) added, and the liquid diluted to 100 c.c. and examined in the spectrophotometer, using the portion 115—125 of the micrometer when the D-ray is at 80°.   T. A. H.

The Mercury Content in the Air, Dust, etc., of Places where Metallic Mercury is in Use. ARVID BLOMQUIST (*Ber. Deut. pharm. Ges.*, 1913, **23**, 29—46).—The mercury vapour contained in the air of rooms where mercury or its preparations are constantly being used is estimated by evolving chlorine, and so converting the mercury into the chloride. Four thousand litres of the air are then drawn through a series of absorbers, two of which contain 100 c.c. of 5% hydrochloric acid, containing 1% of stannous chloride; the third contains 100 c.c. of 5% aqueous potassium hydroxide. The mercury is then estimated by means of a slight modification of Farup's method (intended for urines). A large number of experiments are communicated showing the quantity of mercury found in the air and dust of laboratories and in the urine of the persons employed there, mostly fractions of a milligram.   L. DE K.

New Method for the Estimation of Mercury in Urine and in the Tissues. HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1913, **83**, 249—303).—See this vol., i, 318.

Comparison of Farup's and Schumacher-Jung's Methods for the Estimation of Mercury in Urine. WILHELM BECKERS (*Arch. Pharm.*, 1913, **251**, 4—7).—Farup's method (collecting and weighing the mercury on a gilt asbestos filter after it has been reduced to the metallic state) yields results which agree closely with those obtained by the Schumacher-Jung method (A., 1903, ii, 44), and the methods are equally trustworthy.   W. P. S.

Application of Diphenylcarbazide as Indicator in the Titration of Iron with Dichromate. O. L. BARNEBEY and S. R. WILSON (*J. Amer. Chem. Soc.*, 1913, **35**, 156—162).—Brandt (A., 1906, ii, 309) has suggested the use of diphenylcarbazide as an indicator in the titration of iron. On applying this method, concordant results could not be obtained, and the present investigation was therefore undertaken.

It has been found that the variation in the results is due to the indicator itself, which is oxidised by the dichromate during the titration, 3 mols. of diphenylcarbazide requiring 2 mols. of potassium dichromate for their oxidation.

If a blank experiment is carried out to ascertain the reducing power of the indicator, the method is rendered applicable to the estimation of iron in ores. The end-point is excellent, and small quantities of iron can be estimated as accurately as by the more common methods.   E. G.

Estimation of Iron in Presence of Organic Substances. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1913, **83**, 159—164).—A critical study of the difficulties experienced in estimating iron in

association with proteins or other organic substances. The iron is converted by fusion with a mixture of alkali nitrate and carbonate into oxide, the fused mass dissolved in water, and the iron oxide collected on an ash-free filter. It is advantageous to carry out the washing with a 10—15% solution of ammonium nitrate, and finally to fill the filter with alcohol. A further difficulty is often experienced in removing all traces of iron oxide from the platinum dish.

The method of estimation of iron as ferric phosphate is examined and found to be very unsatisfactory. Washing the ferric phosphate precipitate with ammonium acetate does not remove the difficulties.

E. F. A.

The Separation of Iron and Manganese. F. H. CAMPBELL (*J. Soc. Chem. Ind.*, 1912, **32**, 3—4).—The cold solution of iron and manganese salts, preferably the sulphates, is almost neutralised with ammonia, and a mixture of equal volumes of a 25% potassium iodide solution and a saturated solution of potassium iodate then added. Ferric hydroxide is precipitated by the hydrolysis of the ferric salt, the hydrolysis being made complete because of the removal of the acid formed by the mixture of iodide and iodate, with liberation of iodine. After allowing the precipitate to settle, the liberated iodine is removed by a slight excess of 20% sodium thiosulphate solution. The precipitate is collected, washed first ⁄ with cold and finally with boiling water, and the manganese determined directly in the filtrate as pyrophosphate (compare Gooch and Austin, A., 1899, ii, 128). When metals such as calcium and magnesium are present, the manganese should be separated as sulphide, re-dissolved in acid, and then precipitated as the phosphate. Nickel, cobalt, and zinc do not interfere on account of the solubility of their phosphates in ammonia.

So long as the conditions given above are observed, the results for manganese are accurate, one precipitation only being necessary. Hot solutions cannot be used, since manganese is then precipitated with the iron. If the precipitate of ferric hydroxide is ignited and weighed, the results, for some unknown reason, are high; the precipitate should be dissolved, the ferric salt reduced, and then titrated with permanganate or dichromate.

In the tests carried out, the mixtures contained 0·0287—0·2300 gram of iron, and 0·0328—0·2628 gram of manganese. T. S. P.

Analysis of Ferro-Zirconium. MAX WUNDER and B. JEANNERET (*Zeitsch. anal. Chem.*, 1913, **52**, 99—101).—A reply to the criticism of Weiss and Trautmann (A., 1912, ii, 495). The authors uphold the accuracy of their process (*ibid.*, ii, 96), which is now used exclusively by many works chemists. L. DE K.

The Direct Volumetric Estimation of Tin. HENRY J. B. RAWLINS (*Chem. News*, 1913, **107**, 53—55).—The author recommends the well-known titration with iodine or with ferric chloride in the assay of commercial tin. The titanium chloride process (estimation of excess of iron added) may also be used. The standard solutions

should be checked against a known weight of pure tin dissolved in hydrochloric acid in a current of carbon dioxide. The presence of antimony causes the results to be slightly in excess of the truth and, in delicate assays, it should be determined and allowed for.

The author thinks the titration results are more trustworthy than a gravimetric assay based on an estimation of the impurities.

L. de K.

New Colorimetric Method for Titanium. VICTOR LENHER and W. G. CRAWFORD (*J. Amer. Chem. Soc.*, 1913, **35**, 138—145).— The most generally applicable method hitherto proposed for the estimation of small quantities of titanium is Weller's colorimetric method (A., 1883, 381), in which hydrogen peroxide is employed.

A study of the behaviour of a large number of organic compounds with titanium in concentrated sulphuric acid has shown that distinctive colorations are produced by thymol, phenol, quinol, salicylic acid, and chromotropic acid. Of these, thymol has proved to be the most satisfactory for detecting and estimating small amounts of the metal. The intensity of the coloration is at least 25 times as great as that produced by the hydrogen peroxide method. The colour is not affected by diluting the solution with water until the strength of the sulphuric acid is reduced to 79·4%, and beyond this point it fades in a regular manner. When the solution is heated, the colour disappears, but returns on cooling, and is not permanently discharged until the solution is heated to 100°. The colour is bleached by fluorides or hydrofluoric acid. Chlorides, phosphates, and tin do not affect the intensity, but tungstic acid reduces it in direct proportion to the amount of tungsten present.

In order to apply the test, the substance containing titanium is fused with potassium hydrogen sulphate; the product is dissolved in concentrated sulphuric acid, an excess of thymol in sulphuric acid is added, the solution diluted to a definite volume, and the colour compared in a colorimeter with that given by a standard titanium solution. The method is simple and rapid, and can be applied to smaller quantities of titanium than can be estimated by Weller's method.   E. G.

Use of Cupferron in Quantitative Analysis [of Titanium] ITALO BELLUCCI and L. GRASSI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 30—34. Compare Baudisch, A., 1911., ii, 939).—When an aqueous solution of cupferron is added to an acid solution of titanium chloride or titanium sulphate, the canary-yellow salt, $(NO·NPh·O)_4Ti$, is precipitated quantitatively. If the precipitate is filtered off, dried and ignited (TiO_2 being formed), the process forms a very accurate and convenient means of estimating titanium. Very good results have also been obtained in the application of the method to the separation of titanium from aluminium.   R. V. S.

Estimation of Bismuth by Titration of the Hydrochloric Acid Solution of Bismuth Oxyiodide by Means of Alkalis. C. REICHARD (*Pharm. Zentr.-h.*, 1913, **54**, 103—104).—The process is

intended for the evaluation of bismuth oxynitrate. 0·4 Gram of the powder is dissolved in 10 c.c. of 25% hydrochloric acid, 2 grams of potassium iodide are added, and the liquid diluted to 100 c.c. Twenty-five c.c. of the solution are then titrated with $N/2$-sodium hydroxide until the yellow colour has disappeared. The difference between the alkali used and that required to neutralise the acid represents the bismuth; 2 mols. of sodium hydroxide $= 1$ mol. of bismuth oxide. L. DE K.

The Reaction between Formaldehyde and Bismuth or Copper in the Presence of Strong Alkali. FRANZ HARTWAONER (*Zeitsch. anal. Chem.*, 1913, 52, 17—20).—Bismuth chloride may be reduced to metal by heating with a large excess of both formaldehyde and aqueous sodium hydroxide. If only theoretical quantities are used, or when the liquid is too much diluted, the reduction is very imperfect. Copper, however, is more readily reduced to metal. In the presence of a large excess of alkali, hydrogen is also evolved.

The author also investigated the action of chloral hydrate and acetaldehyde on some metals. In alkaline solution, gold is completely reduced, and should it become colloidal, it may be precipitated by boiling with excess of dilute sulphuric acid. Acetaldehyde also reduces gold in acid solutions. Copper salts are reduced to metal by chloral hydrate in presence of alkali; the metal, however, is very liable to oxidation; acetaldehyde causes no reduction, but, on boiling, copper oxide separates. Bismuth chloride in the presence of alkali is reduced very slowly and incompletely by chloral hydrate, but not by acetaldehyde. Silver salts are completely reduced in alkaline solutions both by chloral hydrate and acetaldehyde; here the latter is to be preferred in practice.
L. DE K.

Estimation of Tantalic Acid and Columbic Acid in Tantalites, Columbites, Yttrotantalites and Fergusonites, and the Colorimetric Estimation of Columbium. E. MEIMBERG (*Zeitsch. angew. Chem.*, 1913, 26, 83—85).—The principle of the method is as follows. The mineral is decomposed by fusion with potassium hydrogen sulphate. The fusion is digested with hydrochloric acid, the residue of mineral acids neutralised with ammonia, and then digested with ammonium sulphide at a gentle heat for twenty-four hours. The residue is collected, washed successively with hot water and boiling, dilute hydrochloric acid, and then dissolved in excess of hydrofluoric acid. The tantalum is then precipitated as potassium tantalum fluoride, K_2TaF_7, by the addition of a concentrated solution of potassium hydrogen fluoride, the columbium remaining in solution. The filtrate from the precipitate is evaporated to dryness, digested with strong sulphuric acid, boiled with water to remove the sulphuric acid, dissolved in hydrofluoric acid, and again precipitated with potassium hydrogen fluoride in order to remove any tantalum still remaining. This process is repeated until the tantalum is completely separated from the

columbium. The potassium tantalum fluoride ie then converted into the pentoxide and weighed as such. It generally contains some titanium, which must be estimated colorimetrically.

For the estimation of the columbium, all the hydrofluoric acid filtrates are evaporated to dryness, and then again taken down with strong sulphuric acid. The residue is treated successively with boiling water, ammonia, ammonium sulphide, and very dilute hydrochloric acid, and weighed as columbium pentoxide.

Gallotannic acid has hitherto been used in testing colorimetrically for columbic acid, but the colour is affected considerably by the presence of tantalum. The author makes use of the fact that the columbates, especially the fluoride compounds, are reduced by tin and hydrochloric acid to coloured products, whereas the tantalates are not affected. The potassium tantalum fluoride, which is to be tested for columbium, is dissolved in dilute hydrochloric acid containing some hydrofluoric acid, and the eolution evaporated down until a copious precipitation of potaesium tantalum fluoride has occurred. After cooling, the crystals are collected and washed with cold dilute hydrofluoric acid. The columbium, together with some tantalum, is in the filtrate, which is evaporated to dryness on the sand-bath. The residue is diesolved in concentrated hydrochloric acid, the solution placed in a colorimeter tube, and reduced with tin. The reduction ie complete in about fifteen minutes, and the colour is then compared with that of a standard, which must be freshly made for each determination. The solutions to bs estimated, as also the standard, should not contain more than 0·1% of columbium. By this method 0·01—0·005% of columbium can readily be estimated. T. S. P.

Delicate Colour Reactions of Gold Salts. JOHN EDWARD SAUL (*Analyst*, 1903, **38**, 54).—If a 0·1% solution of either of the following substances, quinol, pyrogallol, gallotannic acid, *p*-hydroxyphenylaminoacetic acid, salte of phenylhydrazine, 3:4-diaminophenol (amidol), the monomethyl derivatives of *m*- and *p*- (metol) and *o*-aminophenol, associated with quinol in (ortol) and *m*-phenylenediamine, is added to ten volumee of a 0·002% solution of gold chloride, a colloidal solution of gold is formed, presenting a beautiful violet colour varying in intensity and shade with the reagent used. Gallotannic acid gradually produces a rose colour. The author recommends *p*-phenylenediamine as a suitable test for traces of gold. The coloration is at first of a dark green, and still shows with a 0·0001% eolution. After some time the colour undergoes changes. L. DE K.

Estimation of Palladium and its Separation from Copper and Iron. MAX WUNDER and V. THÜRINGER (*Zeitsch. anal. Chem.*, 1913, **52**, 101—104).—To the solution is added a 1% solution of dimethylglyoxime in dilute hydrochloric acid; should ferric chloride be present, a large excess should be added, owing to reduction taking place. The precipitation of the palladium compound is favoured by gentle boiling, and the precipitate is then converted into metal by ignition, with the usual precautions.

From the filtrate the copper is precipitated as thiocyanate by addition of sulphur dioxide and potassium thiocyanate, and weighed as such. The filtrate contains the iron, which is first precipitated with ammonium sulphide and finally weighed as oxide.

L. DE K.

A Source of Error in the Determination of "Permanganate Absorbed" by Drinking Waters by Schulze's Method. LEO GRÜNHUT (*Zeitsch. anal. Chem.*, 1913, **52**, 36–40).—This method (boiling with alkaline permanganate and titrating the excess) is affected when the water itself contains manganese. This, however, may be remedied as follows: To 120—150 c.c. of the sample is added 0·6—0·75 c.c. of 33% aqueous sodium hydroxide, and after shaking a few times and waiting for a few minutes, the precipitate, which also contains the manganese, is filtered off through a Gooch crucible, and 100·5 c.c. of the clear filtrate are then boiled with permanganate as usual. L. DE K.

A Method of Analysing Mixtures of Hydrogen and the Gaseous Saturated Hydrocarbons, Hydrogen, Methane, Ethane, and Propane. PAUL LEBEAU and A. DAMIENS (*Compt. rend.*, 1913, **156**, 144—147; 325—327).—Taking advantage of the fact that, of the four gases under consideration, only hydrogen and methane have any appreciable vapour tension at −190°, the authors first liquefied the gaseous mixture, and then submitted it to fractional distillation, by means of a mercury pump, at −190°. The volatile portion contained the hydrogen and methane, and was analysed eudiometrically, the ethane and propane being pumped off at higher temperatures. By an examination of more complex mixtures, the authors have determined conditions of temperature favourable for a practical separation of other gaseous hydrocarbons from hydrogen.

In the second paper, the mixture studied contained ethane, propane, and *iso*butane, and it was found that by maintaining the mixture at −127° and pumping off all the gas possible, all the ethane and a portion of the propane were removed and could be analysed eudiometrically, the residual liquid containing the remainder of the propane, and all the *iso*butane being pumped off at a higher temperature and similarly analysed. In general, by a study of the vapour tension of the hydrocarbons when liquefied, it is possible, by suitable choice of temperatures, to separate mixtures into fractions containing only two of the hydrocarbons, the fractions then being analysed eudiometrically. W. G.

Estimation of Glyceryl Acetate in Essential Oils. S. GODFREY HALL and ARTHUR J. HARVEY (*J. Soc. Chem. Ind.*, 1912, **32**, 61—62).—The method depends on the separation of the glycerol and its estimation by the triacetin method. A quantity of not less than 10 grams of the essential oil is saponified by heating with alcoholic potassium hydroxide solution, and the solution is then neutralised with hydrochloric acid. After the alcohol has been

removed by evaporation to dryness, the residue is dissolved in a small quantity of water, and the oily portion is separated by extraction with ether. The aqueous solution is then evaporated to a syrupy condition, and the glycerol in it is estimated in the usual way by the triacetin method.   W. P. S.

Detection of Pentoses in Urines containing Dextrose.
ADOLF JOLLES (*Zeitsch. anal. Chem.*, 1913, **52**, 104—108).—To 100 c.c. of diabetic urine (containing up to 5% of dextrose) are added 4 grams of phenylhydrazine hydrochloride and 8 grams of sodium acetate (sugar-free urine is mixed with 1% of dextrose). The whole is heated for an hour in the boiling water-bath and then rapidly cooled. The deposit is collected on a filter and well drained. It is then removed from the filter into a beaker, 15 c.c. of hot water are added, and the whole heated for five minutes on a boiling water-bath. After filtering rapidly, the liquid, which contains the pentosazone, is distilled with addition of 6 c.c. of fuming hydrochloric acid, and 6 c.c. are collected in a test-tube. Three c.c. of the distillate are then mixed with 5 c.c. of Bial's reagent (1 gram of orcinol, 500 c.c. of 30% hydrochloric acid, 30 drops of officinal ferric chloride), and boiled for a short time. In the presence of as little as 0·05% of pentoses, a distinct green coloration is noticed.

When testing urines with more than 5% of dextrose, the amount of the reagents should be doubled.   L. DE K.

Estimation of Dextrose in Urine. K. K. JÄRVINEN (*Zeitsch. anal. Chem.*, 1913, **52**, 14—15).—The dark colour obtained with diabetic urines on heating with alkaline bismuth solution (Almen-Nylander's process) is matched by means of a series of tubes containing increasing quantities of dextrose added to sugar-free urine. If much dextrose should be present in the sample, it must be suitably diluted, and the sugar-free urine likewise.   L. DE K.

Estimation of Reducing Sugars by Lehmann's Method.
LÉON GRIMBERT (*J. Pharm. chim.*, 1913, [vii], **7**, 105—109; *Bull. Soc. chim.*, 1913, [iv], **13**, 117—120. Compare A., 1898, ii, 264, 535;. 1899, ii, 529).—Modifications of Lehmann's method proposed by Riegler and Maquenne (*loc. cit.*) are open to the objection that the solution has to be filtered before the titration, or that the titration has to be carried out in a relatively concentrated solution; further, the time of boiling the sugar solution with the reagent varies in each method. Garnier's modification of the method (A., 1899, ii, 701) lengthens and complicates the process. The author recommends that, after the sugar solution has been boiled for three minutes with a definite volume of Bertrand's reagent (A., 1907, ii, 136), the whole solution should be diluted to 200 c.c. with boiled water, filtered, and the excess of copper in an aliquot portion of the filtrate titrated with thiosulphate solution after the addition of sulphuric acid and potassium iodide. It is preferable to add an excess of thiosulphate solution, and to titrate this with $N/10$·

iodine solution. The copper sulphate solution used is standardised in the same way.　　　　　　　　　　　　　　　　　　　W. P. S.

Quantitative Study of Some Aldehyde Reactions. B. G. FEINBERG (*Amer. Chem. J.*, 1913, **49**, 87—116).—This investigation was undertaken with the object of determining the best methods for estimating various aldehydes. The following methods have been studied: (1) the combination of aldehyde with alkali hydrogen sulphite; (2) the reaction with the normal sulphites; and (3) the precipitation of the aldehydes as hydrazones. These methods have been applied to formaldehyde, benzaldehyde, salicylaldehyde, p-hydroxybenzaldehyde, and vanillaldehyde, and in all cases attempts have been made to establish conditions for the accurate estimation of the compounds.

The compounds of the aldehydes with alkali hydrogen sulphite are resolved into their components by dilute acid or alkali hydroxide, and the readiness with which this decomposition takes place is increased by the presence of a hydroxyl group in proximity to the aldehyde group. Formaldehyde can be estimated accurately by means of alkali hydrogen sulphite, and vanillaldehyde and benzaldehyde can be approximately estimated, but the method does not give satisfactory results with salicylaldehyde, p-hydroxybenzaldehyde, or anisaldehyde.

It has been found that sodium sulphite does not combine with aldehydes with formation of sodium hydroxide, as is generally supposed, but that a reaction takes place on the addition of acid, indicating that sodium hydrogen sulphite is first produced and unites with the aldehyde. Formaldehyde and benzaldehyde can be estimated fairly accurately by means of sodium sulphite, and anisaldehyde can be estimated approximately, but the method is inapplicable to salicylaldehyde, p-hydroxybenzaldehyde, and vanillaldehyde.

Precipitation with p-bromophenylhydrazine gives good results with anisaldehyde, p-hydroxybenzaldehyde, and vanillaldehyde, but not with formaldehyde, benzaldehyde, or salicylaldehyde.

p-Nitrophenylhydrazine has been found generally applicable, and is very suitable for the estimation of vanillaldehyde and p-hydroxybenzaldehyde, whilst with benzaldehyde, salicylaldehyde, and anisaldehyde, it yields results from 2 to 4% too low.

A bibliography of the subject is appended.　　　　　　　E. G.

Estimation of Formaldehyde. GAILLOT (*Ann. Chim. anal.*, 1913, **18**, 17—18).—A definite quantity of the formaldehyde solution under examination is neutralised, treated with an excess of neutralised ammonium sulphate solution, and the resulting acidity of the mixture is titrated (compare this vol., ii, 240); this acidity is equivalent to the amount of formaldehyde present.　　W. P. S.

Detection of Citric Acid in Wine. WILHELM FRESENIUS and LEO GRÜNHUT (*Zeitsch. anal. Chem.*, 1913, **52**, 31—35).—A criticism of some of the processes employed. The following conclusions are

arrived at: (1) The process given by Denigès (based on oxidation and treatment with a mercuric salt) cannot serve to prove the presence of added citric acid in wine. (2) The reaction of Möslinger, as modified by Kries (based on precipitation of potassium hydrogen tartrate by addition of alcohol and precipitating the filtrate, after evaporating off the alcohol and largely diluting with water, with acetic acid and lead acetate), is applicable, and is fairly delicate. (3) The reaction of Schindler (based on the different solubilities of the barium salts of citric and malic acids and sub-sequent use of lead acetate) is only serviceable when large quantities of citric acid are present.   L. DE K.

Hardened (Hydrogenised) Oils and the Detection of **Arachidic Acid.** HANS KREIS and EMIL ROTH (*Zeitsch. Nahr. Genussm.*, 1913, **25**, 81—85).—Sesame, arachis, and cottonseed oils still yield a coloration with Bellier's resorcinol test after they have been "hardened" by treatment with hydrogen in the presence of a catalyst. Hydrogenised whale oil gives an orange colour with this test. The sesamol of sesame oil is not affected by the treatment, and the hydrogenised oil gives the reaction described by Kreis (A., 1904, ii, 75, 790). Arachis oil, either natural or hydrogenised, may be detected in admixtures with other oils by saponifying 20 grams of the oil under examination, separating the solid fatty acids, and dissolving them in 100 c.c. of alcohol; in the case of hydrogenised oils, 200 c.c. of alcohol are required. The boiling solution is then treated with 1·5 grams of lead acetate dissolved in 50 c.c. of alcohol; the precipitated lead soap is collected after about twelve hours, decomposed with hydrochloric acid, and the liberated fatty acids crystallised three times from alcohol, using successively quantities of 50 c.c., 25 c.c., and 12·5 c.c. of alcohol for these operations. Should the oil contain not less than 5% of arachis oil, the fatty acids obtained after the third crystallisation will have m. p. above 70°. This process may be shortened by acidifying the saponified oil with 50% acetic acid, and then adding the lead acetate solution without previously separating the fatty acids.   W. P. S.

Estimation of Caoutchouc in Vulcanised Rubber Materials. PAUL GOLDBERG (*Chem. Zeit.*, 1913, **37**, 85—86).—For the indirect method of estimating caoutchouc, in which the mineral matter present in the material is estimated by ignition and the caoutchouc taken by difference, the following process for estimating the ash is recom-mended, as it prevents certain chemical changes taking place, during the ignition, between the constituents of the ash and the oxygen of the atmosphere. One gram of the sample, previously extracted with acetone, and dried at 50°, is placed in a weighed porcelain boat, which is inserted in a tube through which a current of nitrogen is passed. When all the air has been displaced from the tube, the boat is heated until the caoutchouc melts and distils, and at the end of the operation the mineral matter remaining in the boat is weighed. When the added mineral matter consists of

calcium oxide, magnesium oxide, calcium carbonate, litharge, red lead, lithopone, zinc sulphide, zinc oxide, barium sulphate, silicates, etc., this method of incineration yields trustworthy results, the error not exceeding 0·3%, but when magnesium carbonate is present, the carbon dioxide liberated must be absorbed and estimated. If the rubber material contains "sulphur auratum," the antimony trisulphide is estimated in the ash and calculated into penta-sulphide; cinnabar, if present, is volatilised completely, and must be estimated separately by the method described by Frank and Birkner (A., 1910, ii, 244), and its quantity added to the amount of ash found.   W. P. S.

The **Prussian Blue Reaction.** DANIEL VORLÄNDER (*Ber.*, 1913, 46, 181—192).—The author finds that the reaction between ferric chloride and potassium ferrocyanide is a time-reaction, which is retarded by acid and salts; the extent of the retardation increases with the strength of the acid. In very dilute solutions, such as often occur in analytical practice, it is possible for no blue colour to be produced at all, and only an indefinite green colour after a few hours; after twenty-four hours a few coagulated flocks of Prussian blue may be found.

When a ferrous salt is used instead of ferric chloride the formation of ferrous ferrocyanide is an instantaneous reaction, which is followed by oxidation to Prussian blue by means of the dissolved oxygen. The presence of dilute hydrochloric or sulphuric acid accelerates the formation of a blue colour, as also does the use of excess of the ferrous salt. The test is so delicate that a millimol. of potassium ferrocyanide per litre can be detected.

In carrying out the test for cyanides (or nitrogen) it is best to filter the solution after boiling with ferrous sulphate and sodium hydroxide. The filtrate should then be acidified with dilute hydrochloric acid, and 3—10 drops of fresh ferrous chloride or sulphate added.

Ferrous salts react immediately with potassium ferricyanide, which points to the fact that the slow reaction between ferric salts and potassium ferrocyanide is not due to the formation of a colloidal reaction product, but depends on the condition of the ferric salt solutions.

Examination with the ultramicroscope of the solutions of the various iron salts used, leads the author to the conclusion that solutions of ferric salts may be considered as incomplete colloidal solutions in which the particles are scarcely visible in the ultramicroscope, although much greater than in disperse molecular solutions.

Further experiments with colloidal ferric hydroxide solutions indicate that the colourless solutions obtained by acidifying the colloidal solution prepared from alcoholic ferric chloride and sodium ethoxide are not identical with the colourless solutions obtained from ferric salts and nitric acid. The latter are practically optically clear in the ultramicroscope, whereas the former are seen to consist of colloidal solutions containing large submicrons.   T. S. P.

Rapid Estimation of Tannin Matters and Acidity in Tanning Liquors. RUDOLF VANIČEK (*Zeitsch. angew. Chem.*, 1913, **26**, 68—70).—The process is briefly as follows: The acidity of 50 c.c. of the liquor is taken by means of $N/10$-sodium hydroxide, using phenolphthalein (or phenolphthalein test paper) as indicator, before and after treatment with 50 c.c. of gelatin solution (6 per 1000). The difference in acidity $(a-b)$ is due to the acid principle of the tannin matter.

If a gravimetric analysis of a particular "tannin" has been made, the titre of the soda solution may be found by dividing the number of grams found in 50 c.c. by $(a-b)$. Working with solutions of unknown strength, the result of the titration $(a-b)$ has only got to be multiplied by the titre in order to find the total content in tanning matter.   L. DE K.

Comparative Examination of Methods for the Estimation of Dyes. H. SALVATERRA (*Monatsh.*, 1913, **34**, 255—281).—Knecht's reduction process with titanium chloride and the method elaborated by Pelet-Jolivet and Garuti (A., 1908, ii, 441) for the estimation of pure dyes, dyed silks, and dye vats (waste vat liquors), have been compared, the colouring matters examined being malachite-green, crystal-violet, magenta, naphthol-yellow-S, Martius-yellow, crystal-ponceau-6B, fast-ponceau-B, cotton-scarlet extra, fast-scarlet-PX, orange-G, and orange-GRX. Both methods give satisfactory results when pure materials are to be estimated, although Knecht's process gives values which are too high with malachite-green and too low with orange-G. The trouble experienced in preparing suitable type solutions is, however, a drawback to Pelet's method.

Only Knecht's method gives good results for the titration of dyed silk, and in the case of easily reduced dyes, it may be applied directly. For the examination of waste vat liquors, both methods are trustworthy, whereas colorimetric comparisons with standard solutions are quite impossible. Experiments have been conducted in order to ascertain whether dyes are taken up by silk in molecular proportions, but no such rule could be discovered. It can only be said that with an increase in the number of sulphonic groups, the affinity of silk for the dye diminishes.   J. C. W.

Chemical Detection of Veronal Poisoning. W. MACADIE (*Pharm. J.*, 1913, **90**, 134).—The following methods were employed for the detection of veronal in a suspected case of poisoning by this substance. The stomach wash-out was acidified with hydrochloric acid, shaken out several times with ether, and the ethereal solutions were evaporated; the residue obtained was then extracted with alcohol, the solution evaporated to dryness, the residue dissolved in a small quantity of dilute sodium carbonate solution, filtered, and the filtrate extracted with ether after the addition of hydrochloric acid. On evaporating the ethereal solution, a residue was obtained which was dissolved in a small quantity of alcohol; a portion of this solution was treated with alcoholic sodium hydroxide

solution, heated to remove the alcohol, and the heating then continued until the mixture fused. The fused mass, when treated with sulphuric acid, yielded carbon dioxide and an odour resembling that of a mixture of acetic and butyric acids (compare A., 1911, ii, 670). Another portion of the alcoholic solution was evaporated to dryness, and the residue tested with Millon's reagent in the presence of nitric acid; a gelatinous precipitate, soluble in excess of nitric acid, but not in an excess of the reagent, was obtained. Veronal was also separated from the urine of the patient; for this purpose the urine was treated with calcium chloride to precipitate uric acid, and, after the precipitate had been removed by filtration, the filtrate was acidified and shaken out with ether, the residue of veronal obtained being identified by means of the tests mentioned.

W. P. S.

Rapid Estimation of Pyridine in the Presence of Ammonia in Gas Liquors. OTTO BAESSLER (*J. Gasbeleuchtung*, 1912, 55, 905—906).—The total ammonia and pyridine are first titrated together with standard sulphuric acid; the mixed vapours are then distilled through a warm solution of sodium hypobromite, whereby the ammonia is oxidised to water and nitrogen; the pyridine is carried on into standard sulphuric acid, the excess of which is subsequently titrated. F. M. G. M.

Micro-chemical Tests for the Identification of Some of the Alkaloids. EARL B. PUTT (*J. Ind. Eng. Chem.*, 1912, 4, 508—512).— An account of the preparation, with micro-photographs, of the characteristic crystals formed by alkaloids with certain reagents which affords a ready means for their identification. Alkaloids producing characteristic crystals with iodine are: (1) morphine, shining red plates; (2) codeine, clusters of yellow, blade-like needles; (3) dionine (ethyl-morphine), similar to codeine; (4) atropine, small red crystals, whilst heroine, *apo*morphine, and narcotine furnish amorphous precipitates.

Alkaloids producing characteristic crystals with palladous chloride are (1) morphine, light brown clusters of sheaf-like crystals; (2) codeine yields first a labile form, which rapidly changes to clusters of needles. (3) β-Eucaine, deep yellow characteristic crystals.

Alkaloids yielding characteristic crystals with platinic chloride are (1) cocaine; (2) β-eucaine, clusters of golden (flower) petal-like-crystals; (3) nicotine resembles those obtained with cocaine, but are only formed in neutral or faintly acid solution, whereas the cocaine precipitate is insoluble in acids; (4) antipyrine, yellow, branching, feathery crystals; (5) strychnine, peculiar chisel-shaped clusters which rapidly separate into individual needles; (6) heroine, golden-yellow clusters of needle-like crystals which when fully formed disintegrate. F. M. G. M.

Factors Affecting the Measurements of Absorption Bands. H. HARTRIDGE (*Proc. Roy. Soc.*, 1913, B, 86, 128—140).—In estimating

the absolute value of the carbon monoxide saturation of hæmo-globin, the spectroscopic method is complicated by the fact that each observer must obtain a calibration curve for himself, because individual differences to the threshold values at different wave-lengths occur. These detract from the value also of accurate measurements of absorption bands. Other factors to be considered are the initial intensity of the light and contrast. Provided work is carried out under standard conditions, accurate carbon monoxide estimations are obtainable.   W. D. H.

Behaviour of Copper Salts towards Ganassini's Reagent for Blood. DOMENICO GANASSINI (*Boll. chim. farm.*, 1912, 51, 815—818).—Possible confusion between traces of copper salts and traces of blood (compare Pazienti, this vol., ii, 154) can be avoided by adding to the blue liquid a small quantity of potassium cyanide; if copper is present, the solution at once becomes yellow. Blood does not give this reaction. If copper is absent, the usual blood test is then performed by adding a drop of hydrogen peroxide to the same solution. If copper is present, a trace of potassium cyanide is added to another portion of solution, then the blue reagent, and finally a drop of peroxide; the presence of blood will be indicated by a change of colour from blue to yellow.   R. V. S.

Schardinger's Reaction for Cow's Milk. W. RULLMANN (*Biochem. Zeitsch.*, 1913, 48, 155—156. Compare A., 1911, ii, 667).—A reply to Römer (A., 1912, ii, 610).   S. B. S.

Nephelometry in the Study of Proteases and Nucleases. I. PHILIP ADOLF KOBER (*J. Biol. Chem.*, 1913, 13, 485—498).—At microchemical method for following the digestion of a soluble protein, edestin, based on the use of a nephelometer, is given. This instrument can be easily made from a Duboscq colorimeter. Its readings follow a curve which can be expressed by a mathematical equation.   W. D. H.

The Nature of Peroxydase. WALTHER GRIMMER (*Zeitsch. Nahr. Genussm.*, 1913, 25, 85—88).—The author controverts the statement made by Hesse and Kooper (A., 1912, ii, 1107), that the peroxydase reaction of milk is brought about by the catalytic action of iron salts, such as ferrous lactate. He argues that milk does not contain iron compounds of this type, and that the albumin solutions used in Hesse and Kooper's experiments contained upwards of thirty times more iron than is found in milk. Further, when these iron solutions are heated and then cooled, they regain their power of giving the peroxydase reaction, but such is not the case with milk when it is heated; protein solutions, when mixed with ferrous lactate solution, inhibit the activity of the latter, owing to the formation of insoluble iron-protein compounds. The presence of chloroform, or of mercuric chloride, interferes with and may inhibit the peroxydase reaction of milk.   W. P. S.

INSTRUCTIONS TO ABSTRACTORS,

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

THE object of the abstracts of chemical papers published elsewhere than in the Transactions of the Society is to furnish the Fellows with a concise account of the progress of chemical science from month to month. It must be understood that as the abstracts are prepared for the information of the Fellows in general, they cannot possibly be made so full or so detailed as to obviate on the part of those who are engaged on special investigations the necessity of consulting the original memoirs.

1. Titles of papers must be given literally.

2. Before beginning to write the abstract, the whole of the original paper must be read, in order that a judgment may be formed of its importance and of the scale on which the abstract should be made.

3. In the case of papers dealing with subjects not strictly chemical, the abstract should refer only to matters of chemical interest in the original.

4. The abstract should consist mainly of the expression, in the abstractor's own words, of the substance of the paper.

5. The abstract should be made as short as is consistent with a clear and accurate statement of the author's results.

6. A concise statement showing the general trend of the investigation should be given at the commencement of those abstracts where the nature of the original permits of it.

7. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should, as a rule, be made of this fact.

8. Matter which has appeared once in the *Abstracts* is not to be abstracted again, a reference being given to the volume in which the abstract may be found.

9. As a rule, details of methods of preparation or analysis, or generally speaking of work, are to be omitted, unless such details are essential to the understanding of the results, or have some independent value. Further, comparatively unimportant compounds, such as the inorganic salts of organic bases or acids, should be mentioned quite shortly. On the other hand, data such as melting and boiling points, sp. gr., specific rotation, &c., must be given in every case unless recorded in earlier papers.

Nomenclature.

10. Employ names such as *sodium chloride, potassium sulphate* for inorganic compounds, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chlorides, sulphurous and sulphuric acids.

11. Term compounds of metallic radicles with the OH-group *hydroxides* and not hydrates, the name hydrate being reserved for compounds supposed to contain water of combination or crystallisation.

12. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as sodium hydrogen sulphate, disodium hydrogen phosphate. &c., to the acid salts. Basic salts as a rule are best designated merely by their *formulæ*.

13. Names in common use for oxides should be employed, for example: NO, nitric oxide; CO_2, carbon dioxide; P_4O_{10}, phosphoric oxide; As_4O_6, arsenious oxide; Fe_2O_3, ferric oxide.

14. In open chain compounds, Greek letters must be used to indicate the position of a substituent, the letter a being assigned to the first carbon atom in the formula, except in the case of CN and CO_2H, for example, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2I$ a-iodohutane, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CN$ a-cyanopropane.

15. Isomeric open chain compounds are most conveniently represented as substitution derivatives of the longest carbon chain in the formula; for example,

$$CH_3 \cdot CH_2 {>} CH \cdot CH {<} CH_3 \quad \text{or} \quad CH_3 \cdot CH_2 \cdot CHMe \cdot CHMe \cdot CH_3$$
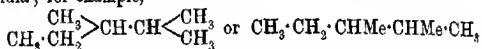
should be termed $\beta\gamma$-dimethylpentane, not methylethyl*iso*propylmethane, and $CH_3 {>} CH \cdot CH {<} CH_3 \quad \text{or} \quad CH_3 \cdot CHMe \cdot CHMe \cdot CO_2H$ should be termed $a\beta$-dimethylbutyric acid, not $a\beta\beta$-trimethylpropionic, or a-methyl*iso*valeric, or methyl*iso*propylacetic acid.
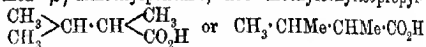
16. Use names such as methane, ethâne, &c., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3 \cdot [CH_2]_5 \cdot CH_3$, &c. Term the hydrocarbons C_2H_4 and C_2H_2 ethylene and acetylene respectively (not ethene and ethine). Homologues of the ethylene series are to be indicated by the suffix *-ene*, and those of the acetylene series, wherever possible, by *-inene*. Adopt the name allene for the hydrocarbon $CH_2 \cdot C \cdot CH_2$.

17. Distinguish all hydroxyl derivatives of hydrocarbons by names ending in *ol*. Alcohols should be spoken of as mono-, di-, tri-, or n-hydric, according to the number of OH-groups. Compounds which are not alcohols, but for which names ending in *ol* have been used, are to be represented by names ending in *ole*, if a systematic name cannot be given, thus anisole not anisol, indole not indol. Compounds such as MeONa, EtONa, &c., should be termed sodium methoxide, sodium ethoxide, &c.

18. The radicles indicated in the name of a compound are to be

given in the order fluoro-, chloro-, bromo-, iodo-, nitro-, nitroso-, amino-, imino-, cyano-, thiocyano-, hydroxy-, keto-.

19. Compounds analogous to the acids of the lactic series containing the OH-group should be termed *hydroxy*-derivatives, and not oxy-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups OEt, OPh, OAc, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus a-ethoxypropionic acid, $OEt \cdot CHMe \cdot CO_2H$, instead of ethyl-lactic acid; 3:4-diethoxybenzoic acid, $(OEt)_2 C_6 H_3 \cdot CO_2H$, instead of diethylprotocatechuic acid; and a-acetoxypropionic acid, $OAc \cdot CHMe \cdot CO_2H$, instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, thus, $C_6 HEt_2(OH)_2 \cdot CO_2H$, and not $C_6 H_3(OEt)_2 \cdot CO_2H$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6 HBr_2(OH)_2 \cdot CO_2H$.

20. The term *ether* should be restricted to the oxides of hydrocarbon radicles and their derivatives, and the esters (so-called compound ethers or ethereal salts) should be represented by names similar to those given to metallic salts.

21. When a substituent is one of the groups NH_2, NHR, NR_2, NH or NR, its name should end in *ino*; for example, β-aminopropionic acid $NH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, β-anilino-acrylic acid, $NHPh \cdot CH \cdot CH \cdot CO_2H$ a-iminopropionic acid, $NH \cdot CMe \cdot CO_2H$.

22. Compounds of the radicle SO_3H should, whenever possible, be termed sulphonic acids, or failing this, sulpho-compounds; for example benzenesulphonic acid, sulphobenzoic acid.

23. Basic substances should invariably be indicated by names ending in *ine*, as aniline instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteins, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

24. The Collective Index, 3rd decade (1893–1902) should be adopted as the standard of reference on questions of nomenclature not provided for in the preceding sections.

Notation.

25. In empirical formulæ the elements are to be given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

26. Equations should be omitted unless essential to the understanding of the results; as a rule, they should not be written on a separate line, but should "run on" with the text.

27. To economise space, it is desirable:

    (a) That *dots* should be used instead of *dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula.

(b) That formulæ should be shortened by the judicious employment of the symbols Me for CH_3, Et for C_2H_5, Pr^a for $CH_2 \cdot CH_2 \cdot CH_3$, Pr^β for $CH(CH_3)_2$, Ph for C_6H_5, Py for C_5H_4N, Ac for $CO \cdot CH_3$, and Bz for $CO \cdot C_6H_5$.

(c) That formulæ should be written *in one line* whenever this can be done without obscuring their meaning.

28. In representing the constitution of benzene derivatives, the relative positions of the radicles in the symbol of benzene should be indicated by numerals, instead of by means of the hexagon formula.

(a) The abbreviations *o-*, *m-*, and *p-*, should be used in place of 1 : 2- or ortho-, 1 : 3- or meta-, and 1 : 4- or para.

(b) In numbering positions in the case of substitution derivatives of phenol, aniline, benzonitrile, benzoic acid, benzenesulphonic acid, benzaldehyde, and toluene, the characteristic radicle of each of these parent substances is to be regarded as in position 1 (compare Collective Index).

(c) Names of substitution derivatives should be given in such a way that the position of the substituent is indicated by a numeral prefixed ; for example :—

SO$_3$H / Br is 2 : 5-dibromobenzenesulphonic acid ;

Me / NH$_2$ is 3-bromo-*o*-toluidine-5 sulphonic acid.
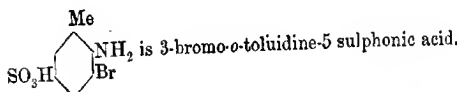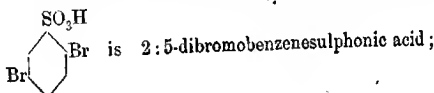
29. In representing the constitution of derivatives of other "closed chain" hydrocarbons, graphic formulæ should not be employed, but the system of numbering positions indicated in Richter's *Lexikon der Kohlenstoff-Verbindungen* (2nd edition, 1899, pp. 16—26) should be used, of which the following schemes may be regarded as typical :—
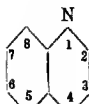

Furan. Thiophen. Pyrrole.

Oxazole. Thiazole. Pyrazole.
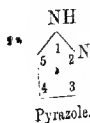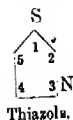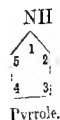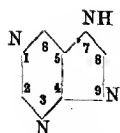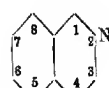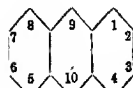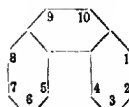
Purine.*

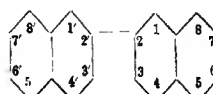Pyridine.

Indole.

Naphthalene.

Quinoline.

*iso*Quinoline.

Anthracene.

Phenanthrene.

Diphenyl.

ββ-Dinaphthyl.

Manuscript.

30. In view of the difficulty of dealing with MSS. of widely varying sizes, abstracts cannot be accepted unless written on quarto paper (10 × 8 in.).

31. Not more than one abstract must appear on a sheet.

32. When an abstract exceeds a sheet in length, the sheets must be fastened together by means of gum at the top left-hand corner.

33. The name of the abstractor must be written diagonally at the top left-hand corner of the first sheet of the abstract.

Proofs.

34. Abstractors are expected to read and correct proofs carefully, and to check all formulæ and figures against MSS.

35. All proofs, however small, must be returned to the Sub-Editor not later than 24 hours after receipt from the printers.

∗∗∗ The Editor's decision, in all matters connected with the Abstracts, must be considered final.

* This numbering, proposed originally by E. Fischer, is adopted in the text of the *Lexikon.*

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

ABBREVIATED TITLE.	JOURNAL.
Amer. Chem. J. . .	American Chemical Journal.
Amer. J. Pharm. . .	American Journal of Pharmacy.
Amer. J. Physiol. . .	American Journal of Physiology.
Amer. J. Sci. . .	American Journal of Science.
Anal. Fis. Quim. . .	Anales de la Sociedad Española Fisica y Quimica.
Analyst . . .	The Analyst.
Annalen . . .	Justus Liebig's Annalen der Chemie.
Ann. Physik . .	Annalen der Physik.
Ann. Chim. anal. . .	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Phys. . .	Annales de Chimie et de Physique.
Ann. Inst. Pasteur .	Annales de l'Institut Pasteur.
Ann. sci. Univ. Jassy .	Annales scientifiques de l'Université de Jassy.
Arch. expt. Path. Pharm. .	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Hygiene . .	Archiv für Hygiene.
Arch. Néerland. . .	Archives Néerlandaises des sciences exactes et natur. elles.
Arch. Pharm. . .	Archiv der Pharmazie.
Arch. Sci. phys. nat. . .	Archives des Sciences physiques et naturelles.
Arkiv Kem. Min. Geol. .	Arkiv för Kemi, Mineralogi och Geologi.
Atti R. Accad. Sci. Torino.	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei .	Atti della Reale Accademia dei Lincei.
Beitr. chem. Physiol. Path. .	Beiträge für chemische Physiologie und Pathologie.
Ber. . . .	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. bot. Ges. .	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. pharm. Ges. .	Berichte der Deutschen pharmazeutischen Gesellschaft.
Ber. Deut. physikal. Ges. .	Berichte der Deutschen physikalischen Gesellschaft.
* *Bied. Zentr.* . .	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bio-Chem. J. . .	The Bio-Chemical Journal.
Bio-chem. Zeitsch. .	Biochemische Zeitschrift.
Boll. chim. farm. .	Bollettino chimico farmaceutico.
Bull. Acad. roy. Belg. .	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow .	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Assoc. chim. Sucr. Dist.	Bulletin de l'Association des chimistes de Sucrerie et de Distillerie.
Bull. Coll. Agr. Tōkyō .	Bulletin of the College of Agriculture, Imperial University, Tōkyō.
Bull. Geol. Soc. Amer. .	Bulletin of the Geological Society of America.
Bull. Imp. Inst. .	Bulletin of the Imperial Institute.
Bull. Soc. chim. .	Bulletin de la Société chimique de France.
Bull. 'Soc. chim. Belg. .	Bulletin de la Société chimique de Belgique.
Bull. Soc. franç. Min. .	Bulletin de la Société française de Minéralogie.
Bull. Soc. ind. Mulhouse. .	Bulletin de la Société industrielle de Mulhouse.
Centr. Bakt. Par. .	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Min. . .	Centralblatt für Mineralogie, Geologie und Palaeontologie.
* *Chem. Zentr.* . .	Chemisches Zentralblatt.

* Abstracts from the *Zentralblatt* are made only in the case of papers published in journals other than those included in this list.

ABBREVIATED TITLE.	JOURNAL.
Chem. News . . .	Chemical News.
Chem. Rev. Fett-Harz-Ind.	Chemische Revue über die Fett- und Harz-Industrie.
Chem. Weekblad .	Chemisch Weekblad.
Chem. Zeit. . .	Chemiker Zeitung.
Compt. rend. . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Exper. Stat. Record .	Experiment Station Record.
Gazzetta . . .	Gazzetta chimica italiana.
Geol. Mag. . . .	Geological Magazine.
Jahrb. Min. . .	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil.-Bd. .	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
Jahrb. Radioaktiv. Elektronik.	Jahrbuch der Radioaktivität und Elektronik.
J. Amer. Chem. Soc. . .	Journal of the American Chemical Society.
J. Biol. Chem. . . .	Journal of Biological Chemistry, New York.
J. Chim. phys. . .	Journal de Chimie physique.
J. Geol. . . .	Journal of Geology.
J. Hygiene . . .	Journal of Hygiene.
J. Inst. Brewing .	Journal of the Institute of Brewing.
J. Landw. . .	Journal für Landwirtschaft.
J. Med. Research .	Journal of Medical Research.
J. Path. Bact. . .	Journal of Pathology and Bacteriology.
J. Pharm. Chim. . .	Journal de Pharmacie et de Chimie.
J. Physical Chem. . .	Journal of Physical Chemistry.
J. Physiol. . . .	Journal of Physiology.
J. Physique . . .	Journal de Physique.
J. pr. Chem. . . .	Journal für praktische Chemie.
J. Roy. Agric. Soc. . .	Journal of the Royal Agricultural Society.
J. Roy. Soc. New South Wales.	Journal of the Royal Society of New South Wales.
J. Russ. Phys. Chem. Soc. . .	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind. . .	Journal of the Society of Chemical Industry.
K. Svenska Vet-Akad. Handl.	Kongl. Svenska Vetenskaps-Akademiens Handlingar.
Lancet.	The Lancet.
Landw. Versuchs-Stat. .	Die landwirtschaftlichen Versuchs-Stationen.
L'Orosi	L'Orosi.
Mem. Accad. Sci. Torino.	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Coll. Sci. Eng. Kyōtō.	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Metallurgie . . .	Metallurgie.
Milch. Zentr. . .	Milchwirtschaftliches Zentralblatt.
Min. Mag. . . .	Mineralogical Magazine and Journal of the Mineralogical Society. .
Monatsh. . . .	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Nuovo Cim. . .	Il Nuovo Cimento.
Pflüger's Archiv . .	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. Arch. .	Pharmaceutical Archives.
Pharm. Centr-h.	Pharmazeutische Centralhalle.
Pharm. J. . .	Pharmaceutical Journal.
Pharm. Rev. . .	Pharmaceutical Review.
Pharm. Weekblad.	Pharmaceutisch Weekblad.
Pharm. Zeit. . .	Pharmazeutische Zeitung.
Phil. Mag. . . .	Philosophical Magazine (The London, Edinburgh and Dublin).

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

ABBREVIATED TITLE.	JOURNAL.
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rend. Accad. Sci. Fis. Mat. Napoli.	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche-Napoli.
Rev. de Métallurgie	Revue de Métallurgie.
Rev. intern. Falsif.	Revue internationale des Falsifications.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Sitzungsber. K. Akad. München.	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften zu München.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Amer. Inst. Mining Eng.	Transactions of the American Institute of Mining Engineers.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Path. Soc.	Transactions of the Pathological Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Tsch. Min. Mitt.	Tschermak's Mineralogische Mitteilungen.
U.S.A. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U.S.A.
U.S.A. Dept. Agric. Rep.	Reports of the Department of Agriculture, U.S.A.
Verh. Ges. deut. Naturforsh. Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
Wiss. Abhandl. Phys.-Tech. Reichsanstalt.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Biol.	Zeitschrift für Biologie.
Zeitsch. Chem. Ind. Kolloide.	Zeitschrift für Chemie und Industrie der Kolloide.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Farb. Ind.	Zeitschrift für Farben-Industrie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie
Zeitsch. prakt Geol.	Zeitschrift für praktische Geologie.
Zeitsch. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie
Zeitsch. wiss. Photograph. Photophysik. Photochem.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Zeitsch. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen.